which is self-explanatory, and are plotted in Fig. 1. In the figure it can be seen that the results from the anode portions are accurately represented by the theoretical line. The results from the cathode portions were subject to a greater error from some unknown cause, but the points are scattered uniformly about the theoretical curve. Some measurements were also made with a still smaller proportion of sodium chloride than those shown in the table, but were not successful. They at least, however, showed movement of sodium-ion constituent in a region of concentrations in which the results of Schneider and Braley would lead one to expect no such movement. It is hoped to continue this research with somewhat changed experimental arrangements, although these experiments, together with the considerations outlined in the preceding article, appear to be ample to decide the matter under discussion.

Conclusion

The results of Schneider and Braley on the transference numbers of sodium- and potassium-ion constituents in a mixture of the chlorides at a total concentration of 0.2 *N* have been repeated, with a modified experimental technique. Their experiments indicated that with a low proportion of sodium chloride the transference number of the sodium-ion constituent drops nearly to zero, a result which has not been confirmed by the experiments described in this paper. Since the new results follow closely the prediction based on the assumption of simple ions, and no ionic complexes, the conclusion of Schneider and Braley that such complexes are present in these solutions is also not confirmed.

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[Contribution from the Fixed Nitrogen Research Laboratory of the United States Department of Agriculture]

THE MECHANISM OF THE FIXATION OF NITROGEN AS SODIUM CYANIDE

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The fixation of nitrogen by a heated mixture of sodium carbonate and carbon, with finely divided iron as a catalyst, is usually represented by the equation, $Na_2CO_3 + N_2 + 4C = 2NaCN + 3CO$. The investigation of this system would be greatly simplified if we could study separately the intermediate reactions leading to the final result expressed by the above equation. This paper describes a series of experiments which, it is believed, establishes the nature of these intermediate reactions.

Those who have speculated on the mechanism of this reaction have generally agreed that metallic sodium is first formed, but varying hypotheses have been advanced regarding the formation of cyanide from the three elements. We might postulate the formation as intermediate compounds of any one or, for that matter, all of the possible compounds containing two of the elements; that is to say, sodium nitride or other sodium nitrogen compounds, cyanogen or sodium carbide. At one time or another, each of these has been suggested as the true intermediate compound in the formation of sodium cyanide from the elements. In addition, sodium cyanamide has sometimes been considered to be a definite intermediate compound. The various theories have been reviewed by Bertelsmann.[1] Berthelot[2] first suggested the hypothesis that sodium carbide is formed, which he supposed might then absorb nitrogen to form sodium cyanide in a manner analogous to the formation of hydrogen cyanide from acetylene and nitrogen in an electric spark.

In the present investigation, Berthelot's hypothesis has been proved to be correct by showing the improbability of the formation of sodium nitride or cyanogen as an intermediate compound and by carrying out experimentally each step necessary to the formation of cyanide through sodium carbide as an intermediate compound.

It appears from these experiments that the formation of sodium cyanide in a system consisting of sodium carbonate, carbon, iron and nitrogen at an elevated temperature takes place chiefly, if not entirely, through the following series of reactions: $Na_2CO_3 \rightleftharpoons Na_2O + CO_2$; $(CO_2 + C \rightleftharpoons 2CO)$; $Na_2O + C \rightleftharpoons 2Na + CO$; $2Na + 2C \rightleftharpoons Na_2C_2$; $Na_2C_2 + N_2 \rightleftharpoons 2NaCN$.

Experimental Part

In the experiments that follow, the general plan has been to take a part only of the reacting constituents which are present in the sodium carbonate-carbon-iron mixture during the formation of sodium cyanide and study the reactions in the simpler systems thus built up. The conditions of these studies have been, as nearly as possible, those prevailing during the formation of cyanide, in order that the results of studies in the simpler systems might indicate the more certainly what takes place in the system: sodium carbonate-carbon-iron-nitrogen.

Attempts to Form Sodium Nitride from the Elements

Both nitrogen and sodium (as will be seen below) are present during the fixation of nitrogen as cyanide, and it was necessary, therefore, to consider the possibility of a reaction between these elements under the conditions prevailing. While it has heretofore been found impossible to obtain sodium nitride directly from the elements, except under the influence of an electric discharge, and while the nitride so obtained was decomposed

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[1] Bertelsmann, "Die Technologie der Cyanverbindungen," Oldenbourg, Berlin, 1906, pp. 81–85.

[2] Berthelot, *Compt. rend.*, **67**, 1141 (1868).

by slight heating,[3] it appeared not impossible that sodium nitride might be formed in the presence of metallic iron as a catalyst at high temperatures and that it might exist in low concentrations in the gas phase in equilibrium with sodium vapor or even in a condensed phase consisting of a melt of sodium carbonate and cyanide with sodium nitride in solution.

To test these possibilities, nitrogen and sodium vapor were heated together under the following conditions. Metallic sodium in an iron boat was placed in an iron tube, 120 cm. long, and heated in an electric tube furnace, 30 cm. long, while a rapid stream of nitrogen was passed through the iron tube. The temperature of the sodium was about 800°, while that of the hottest part of the tube through which the gases passed after leaving the boat was about 1000°. The sublimate from the boat was deposited in the cool end of the long iron tube, which projected about 60 cm. beyond the furnace. After heating, the boat was pulled into the cool inlet end of the iron tube and the whole apparatus cooled by opening the furnace. The boat and the sublimate were then examined for nitride by treating with water and observing whether ammonia was formed, as determined by Nessler's reagent. In one experiment iron was added to the sodium in the boat and the hottest section of the iron tube packed with steel wool. In another, the conditions were similar except that the boat also contained a melt of sodium cyanide and carbonate in about equal proportions.

In no case was even a trace of nitride found either in the boat or in the sublimate. Tests were also made for the only other known compound of sodium and nitrogen, sodium azide (using the ferrous sulfate test[4]), although this compound was even less to be expected than the nitride. It appears justifiable, therefore, to conclude from these experiments and from previous work with the compounds of nitrogen and sodium, that the existence of a sodium-nitrogen compound as an intermediate in the formation of sodium cyanide is improbable.

Cyanogen as an Intermediate Compound

There is no satisfactory evidence that cyanogen, $(CN)_2$, has ever been formed directly from the elements.[5] The free energy of cyanogen is given by Lewis and Randall[6] as 92,000 calories at 25°. While this value was obtained through a series of equilibria and hence may not be accurate, it should be of the right order of magnitude.

From the equations, $\Delta F = -RT\ ln\ K$ and $(\mathrm{d}\,ln K)/\mathrm{d}t) = (Q/RT^2)$, using the above value for ΔF and Thomsen's value of —66,000 calories for Q, the heat of formation of cyanogen, it is calculated that at 1000° there should be in equilibrium with one atmosphere of nitrogen and solid carbon only 10^{-29} atmospheres of cyanogen, a vanishingly small amount.

The conclusion from this calculation that cyanogen is not an intermediate compound in the fixation of nitrogen as cyanide was confirmed by passing

[3] Fischer and Schröter, *Ber.*, **43**, 1465 (1910).

[4] Dennis and Browne, *Z. anorg. Chem.*, **40**, 68 (1904).

[5] Koenig and Hubbuch, *Z. Elektrochem.*, **28**, 202 (1922). Berthelot, *Compt. rend.*, **144**, 354 (1907).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., p. 608, **1923**.

nitrogen through a briquetted mixture of carbon and iron (the iron was included because of any possible catalytic action which it might have), heated at about 1000° in an iron tube, and thence over an iron boat containing metallic sodium at about 750°. Under these conditions the sodium would have absorbed cyanogen if any had been present.[7] Not a trace of cyanide was formed. From these theoretical and experimental considerations the hypothesis that cyanogen is an intermediate in the formation of sodium cyanide appears untenable.

Experiments Showing the Formation of Sodium Cyanide through Sodium Carbide

The Reduction of Sodium Carbonate by Carbon.—The fact that metallic sodium can be produced by direct reduction of the carbonate has long been known.[8] Some experiments were, nevertheless, made to show that this reduction proceeds readily at the relatively low temperature of 900–1000°, necessary for the fixation of nitrogen as sodium cyanide.

In a typical experiment, 18 g. of a briquetted mixture of equal parts of sodium carbonate, carbon (petroleum coke) and iron was heated at 1000° for two hours in a stream of hydrogen, passing at the rate of 0–2 liters per minute. At the end of the experiment, the charge contained only 1.5% of alkali, while large amounts of sodium (and some sodium carbide, as indicated by the acetylene odor on contact with moisture) collected in the cool part of the apparatus. Similar results were obtained with the inert gas, argon.

Distillation of sodium (and sodium carbide) was also often noticed in an extensive series of experiments on the absorption of nitrogen by heated mixtures of sodium carbonate, carbon (including lampblack, metallurgical coke, petroleum coke, wood charcoal) and iron. In these latter experiments, it appeared that the formation of metallic sodium occurred about as readily in charges containing only 1% of iron as in those containing 30%, even though the formation of cyanide was much slower in the charges containing the lower proportion of iron. The experiments on this point were not sufficiently quantitative to permit a statement that the iron has no effect on the reduction of sodium carbonate, but it seems unlikely that it is essential for the reduction.

The Formation of Sodium Carbide from the Elements.—It was next necessary to show that metallic sodium and carbon could react directly to form sodium carbide. The first two experiments were made in such a way that heated carbon was acted upon by sodium vapor at a relatively low pressure.

An iron tube closed at one end and attached at the other to a vacuum pump was heated in an electric tube furnace. In the tube were two iron boats, one containing 5 g. of carbon (petroleum coke) briquets and the other containing 4 g. of metallic sodium,

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[7] Berthelot, *Compt. rend.*, **89**, 63 (1859).

[8] Deville, *Ann. chim. phys.*, **46**, 415 (1856).

the carbon being nearer the vacuum pump. After the tube had been evacuated, the temperature was quickly raised, while the evacuation was continued, until the carbon was at 900° and the sodium at about 800°; these temperatures were maintained for an hour. The two experiments differed only in that in one carbon alone was contained in the second boat, while in the other finely divided iron was mixed with the carbon in order that any catalytic effect which the iron might exert on the formation of sodium carbide might be noted. After the experiment, the tube was sawed into sections and each piece examined. The carbon briquets when wetted gave no odor. The wetting of the tube between the carbon and the end of the furnace attached to the vacuum pump, however, gave an unmistakable odor of acetylene, the same odor that was obtained when the purest sodium carbide available was moistened.

Hence, even with the low partial pressure of sodium vapor which was in contact with the carbon under these conditions, some sodium carbide was formed. It necessarily passed through the vapor phase, since it was found at some distance from the carbon. The presence of iron did not appear to promote the formation of carbide. There was, in fact, no noticeably larger amount of carbide formed in the experiment in which iron was mixed with the carbon.

Further experiments on the formation of sodium carbide from the elements were carried out, in which carbon was exposed to the action of a much higher pressure of sodium vapor.

This apparatus consists essentially of a cylindrical Monel metal container having the inside dimensions 1.6 × 9 cm., and a length of seamless steel tubing having an inside diameter of 1.6 mm. which was attached to the open end of the Monel cylinder by means of a special joint designed to maintain a gas-tight connection at high temperatures and to be detachable after heating.

In the experiments with this apparatus, carbon and sodium were first introduced separately in small boats. The tube was then attached and the apparatus was evacuated. As the temperature was raised, some volatilized sodium condensed in the narrow outlet tube and sealed the apparatus, so that the pressure of sodium vapor could build up. The temperature in these experiments was 900°, at which the vapor pressure of metallic sodium is considerably above one atmosphere. Experiments were made in this way with three types of carbon, namely, petroleum coke, lampblack and metallurgical coke, the samples in all cases passing a 200-mesh sieve. The experiments were further varied in that iron was sometimes added to the carbon and sometimes omitted.

It was found that when petroleum coke or lampblack was used, considerable quantities of carbide were formed, as indicated by the evolution of acetylene. The amounts were markedly greater than in the experiment described above, in which the partial pressure of sodium was lower. There was about equal acetylene evolution from the carbon in the boat and from the walls of the apparatus, so that it appeared likely that at the reaction temperature the carbide had been largely in the gas phase. This is consistent with the later finding that sodium carbide is not stable in the condensed phase at 900°. This point will be shown more fully in a later paper on the thermal dissociation of sodium carbide. There was no detectable amount of carbide formed under the conditions of these experiments when the carbon was supplied in the form of metallurgical coke. This result is of particular interest in connection with the fact that the formation of cyanide in a heated mixture of sodium carbonate, iron and metallurgical coke is very much slower than when other forms of carbon are used. These two facts, considered together, afford strong support to the view that sodium carbide must be formed as a step in the synthesis of sodium cyanide.

In all of these experiments, the presence of iron appeared to make no difference in the amount of carbide formed. It may not be said from these experiments that iron does not facilitate the formation of carbide to a slight extent. It may be confidently stated, however, that iron is not essential to the formation of carbide. Sodium carbide was still formed in an amount apparently as great when pure carbon (lampblack) was contained in a copper boat as when the carbon was mixed with an equal quantity of powdered iron.

In most of these experiments, the odor of acetylene was used for identification of carbide. In one experiment, however, the formation of carbide was confirmed by fitting the Monel cylinder with a 2-hole rubber stopper, and drawing moist air through the cylinder and then through a solution of silver nitrate. A slight but distinct precipitate of silver carbide, Ag_2C_2, was formed.

If sodium cyanamide is an intermediate compound in cyanide formation, we might expect to find a sub-carbide, Na_2C, as the product of reaction of sodium and carbon, since it is difficult to see how cyanamide could be formed preliminarily to cyanide, except by the absorption of nitrogen by such a sub-carbide. It has been seen, however, that the compound of sodium and carbon evolves acetylene and is, hence, the normal carbide, Na_2C_2. It is improbable, therefore, that sodium cyanamide is an intermediate compound.

The Nitrification of Sodium Carbide.—It is to be expected from analogy with other carbides that sodium carbide will absorb nitrogen. It is, perhaps, not entirely obvious that cyanide would be formed rather than the cyanamide or nitride, as is the case with some of the carbides. It has been found in these experiments that nitrogen is absorbed by sodium carbide to form sodium cyanide. A further interesting result is that iron catalyzes the reaction.

Sodium carbide was prepared by a modification of the method of Matignon,[9] according to which acetylene reacts with molten metallic sodium.

The material used contained, by analysis, 76% of sodium carbide, 7.2% of metallic sodium, and 16.8% of carbon (by difference). In these experiments, purified nitrogen was passed at the rate of 0.2 liters per minute for one hour over heated sodium carbide contained in an iron or copper

[9] Matignon, *Compt. rend.*, **124**, 775 (1894).

boat and an examination made, following the experiment, of the contents of the boat and of the material which volatilized into the iron or Pyrex glass furnace tube. The Table I gives the results of the examination of the boat contents after the nitrogen treatment.

TABLE I

THE NITRIFICATION OF SODIUM CARBIDE

A Pyrex tube was used in Expts. 1–7 and an iron tube in Expts. 8–19. The boat was of copper in Expts. 13, 14 and 17 and of iron in the other experiments.

			Boat contents	
Expt.	Temp. °C.	Catalyst	% of Alkali of charge remaining	% of Orig. Na_2C_2 converted to NaCN
1	500	Fe	84	0.39
2	500	..	98	.66
3	600	Fe	53	22.9
4	600	Fe	36	13.2
5	600	..	84	0.57
6	700	Fe	33	10.6
7	700	..	17	0.51
8	700	Fe	35	11.1
9	700	..	47	1.5
10	800	Fe	45	20.5
11	800	..	25	5.4
12	800	..	23	9.0
13	800	..	15	0.55
14	800	..	15	.45
15	900	Fe	35	17.9
16	900	..	4.1	2.8
17	900	..	3.9	0.85
18	1000	Fe	3.6	.24
19	1000	..	2.54	.25

One of the most evident conclusions to be drawn from these results is that iron catalyzes this reaction. Without iron in the charge, there is no appreciable nitrification of sodium carbide below 700° or 800° and then only when the charge is contained in an iron boat. When the iron boat is replaced by one of copper, it is found that at 800° only 0.5% of the sodium carbide is nitrified and 0.85% at 900° as compared with 20.5 and 18%, respectively, for charges containing iron. With iron mixed with sodium carbide in equal proportions, rapid nitrogen absorption is obtained at temperatures as low as 600°. Thus, in Expt. 3 at this temperature, 22.9% of the sodium carbide was converted to sodium cyanide.

This reaction is the only one of the series of reactions leading to the formation of sodium cyanide in which we have been able to note a marked catalytic action of iron. It would appear from this that the chief function of the iron in the fixation of nitrogen as cyanide is to activate nitrogen rather than to serve as a carrier for carbon as has been generally believed.

The thermal dissociation of sodium carbide proceeded simultaneously with the absorption of nitrogen in these experiments. There is, for that reason, no particular significance to the comparison of the percentage of the sodium carbide which is found as sodium cyanide in the boat following experiments at different temperatures. The decomposition pressure of sodium from solid sodium carbide becomes one atmosphere at about 800°. Hence, in these experiments it was possible to get cyanide above this temperature only because an appreciable time is required for the decomposition. At 900° considerable cyanide is formed before decomposition can occur. At 1000°, however, only 0.25% of the sodium carbide was found as cyanide in the boat whether or not iron was present with the carbide. At these higher temperatures, considerable cyanide was found in the sublimate. At 1000°, 4% of the sodium carbide used appeared in the sublimate as cyanide with iron in the carbide and 1.7% without iron.

Since, as we have seen, solid sodium carbide is not stable at 900–1000°, the formation of cyanide must occur by reaction of nitrogen with gaseous sodium carbide under the conditions employed in the fixation of nitrogen as cyanide. From the relative amounts of metallic sodium and sodium carbide found in the sublimate in the above experiments, it appears that the equilibrium, $2Na + 2C \rightleftharpoons Na_2C_2$, is shifted far toward the left in the gas phase at the temperatures used. Some evidence was obtained, however, which indicates that the equilibrium in the gas phase becomes more favorable to the formation of the carbide with increasing temperature. It has also been found that at a temperature of 1000° sodium cyanide is quite appreciably dissociated to sodium carbide and nitrogen. These equilibria will be discussed more fully in a later communication.

It has been found that the absorption of nitrogen takes place without any preliminary dissociation to the elements such as has been found to occur in the case of calcium carbide.[10] To demonstrate this point, a mixture of sodium carbide, iron powder and metallic sodium was placed in the Monel cylinder of the apparatus used in the experiments on the direct reaction of sodium and carbon. In this case, however, the outlet tube was made larger (6 mm. inside diameter), so that it would not become plugged with sodium. This apparatus was filled with purified nitrogen and connected with a manometer. The cylinder was then heated gradually in a small electric furnace. The pressure increased with the temperature, until 650° was reached, when the pressure dropped, going finally below atmospheric, indicating that nitrogen was absorbed. The presence of sodium with the sodium carbide prevented dissociation of sodium carbide and hence the absorption must have been by undissociated sodium carbide.

It is interesting to note that one would expect the compound $Na{-}C{\equiv}N$ from $Na{-}C{\equiv}C{-}Na$, rather than $Na{-}N{=}C$, which is most favored as the structural formula of sodium cyanide.[11] This may perhaps explain

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[10] Krase and Yee, THIS JOURNAL, **46,** 1358 (1924).

[11] Sidgwick, "Organic Chemistry of Nitrogen," Clarendon Press, **1910,** p. 209.

the fact observed by Posnjak and Merwin[12] that the compound present in the product of the cyanide process of nitrogen fixation is crystallographically different from ordinary sodium cyanide.

Acknowledgment.—The authors desire to express their indebtedness to Dr. J. M. Braham for suggestions and criticisms during the progress of this investigation.

Summary

The formation of sodium cyanide in a mixture of sodium carbonate, carbon and iron catalyst when heated in nitrogen takes place through (1) the reduction of sodium carbonate to metallic sodium, (2) the formation of sodium carbide from the elements, and (3) the absorption of nitrogen by (gaseous) sodium carbide to form sodium cyanide.

Iron has been shown to exert a marked catalytic effect on the absorption of nitrogen by sodium carbide, but does not appear to be essential for the reduction of sodium carbonate or for the formation of sodium carbide.

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NOTES

Rapid Corrosion of Metals by Acids within Capillaries.—About eight years ago the writer observed an interesting effect of hydrochloric acid upon iron surfaces in capillary spaces. So far as he is aware, this effect has not been previously described, so he feels that it may be well to present it at this time. The following simple experiment, which has been several times repeated, shows the nature of the effect. A rubber band is wrapped rather tightly about a piece of soft iron. The iron is immersed in dil. hydrochloric acid for a week or two. At the end of this time, the iron will be found to have been eaten away or pitted beneath the rubber. The acid has acted more rapidly within the capillary spaces between the rubber and the metal than it has upon the exposed surfaces. The experiment was modified, with the same result, by clamping two flat pieces of iron together and immersing them in acid. Also, the action was observed visually by using a glass slide attached to a flat piece of iron. Beneath the glass the capillary space was seen to be largely filled with greatly flattened bubbles, the boundaries of which were in slow but constant motion. The bubbles would extend till the edges of the slide were ap-

Original surface.

After pickling in HCl, showing pitting effected beneath a rubber band.

Fig. 1.

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[12] Posnjak and Merwin, *J. Wash. Acad. Sci.*, **9**, 282 (1919).