proper value. Water was added so that in each case the volume was 200 cc. A small excess of 0.1 N potassium dichromate solution was added and the solution allowed to stand for 45–60 minutes. The excess of dichromate was titrated against a standard solution of ferrous iron (ferrous ammonium sulfate), using an Eppley titration apparatus.

A ratio between the potassium dichromate and ferrous iron solutions was determined at the close of each day's work. The dichromate solution was standardized against specially purified tellurium dioxide.

Part 1 of the table shows that tellurium dioxide is quantitatively oxidized to the telluric state by potassium dichromate, and that selenium dioxide has no effect upon the determination. Selenium dioxide in quantities up to .2780 g. does not affect the titration of potassium dichromate by ferrous sulfate.

Part 2 indicates the accuracy of the method for various amounts of tellurium dioxide in the presence of selenium dioxide.

Part 3 indicates that tellurium dioxide may be accurately determined in the presence of both selenium and copper.

Summary

1. Tellurium in large or small amounts may be rapidly and accurately determined by oxidizing with an excess of potassium dichromate and titrating the latter electrometrically with ferrous sulfate.

2. Small amounts of selenium and copper do not interfere with the determination.

ROLLA, MISSOURI

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE THERMAL DISSOCIATION OF SODIUM CARBIDE

BY E. W. GUERNSEY AND M. S. SHERMAN

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It has been recently shown[1] that the fixation of nitrogen as sodium cyanide in a heated system consisting of sodium carbonate, carbon, iron and nitrogen, involves as one step the formation of sodium carbide. It was desirable, therefore, to investigate the conditions of stability of sodium carbide or, more specifically, to study the equilibrium between sodium vapor, carbon and sodium carbide. This paper deals for the most part with the dissociation pressure of sodium from solid sodium carbide. As will be shown, this dissociation pressure becomes one atmosphere below the temperatures used in the commercial production of sodium cyanide, and it would, therefore, be useful in the study of this fixation reaction to have data on the equilibrium between sodium and sodium carbide in the

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[1] Guernsey and Sherman, THIS JOURNAL, **47**, 1932 (1925).

gas phase at these higher temperatures. It has, however, thus far been possible to get only very approximate data on this equilibrium.

Experimental Part

The Preparation of Sodium Carbide.—The sodium carbide used in this study was prepared by bubbling acetylene into molten metallic sodium. This method was used by Matignon[2] but unfortunately he published only very meager experimental details and it was therefore found necessary to develop satisfactory apparatus and technique, a somewhat detailed description of which is given here. Among the difficulties in the development of the method were (1) the tendency for acetylene to decompose to the elements; (2) the extreme hygroscopicity of the product; and (3) the necessity for complete reaction to avoid having to separate sodium from sodium carbide.

The procedure finally adopted is as follows.

About 25 g. of freshly cut metallic sodium is introduced into the tube A (dimensions 5 × 25 cm.) (see Fig. 1) which has been previously filled with purified acetylene. While the temperature of tube A is being raised by means of an oil-bath, purified acetylene is supplied through the hollow stirrer F. This stirrer is held just above the metallic sodium until melting occurs, when it is lowered into the position shown and started rotating at about 120 r.p.m., the mercury seal D serving to connect the fixed to the rotating part of the acetylene inlet.

When the temperature reaches about 120°, a fine powder varying in color from white to dark purple commences to form with an evolution of heat and consequent rise in temperature, as indicated by the thermometer G. At about 150°, the oil-bath is removed and the temperature maintained at 150–200° by regulating the flow of acetylene. After about an hour and a half, the reaction slackens and the temperature drops. The entire contents of the flask should now be in the powdered state and moving about freely under the action of the stirrer. The bulk of the powder at this point is about four times that of the sodium used. After further heating by the oil-bath at 190–195° for three or four hours, during which time the powder becomes practically white, the charge is cooled and tested for metallic sodium (development of a blue color by suspending it in dry liquid ammonia). If any sodium remains, the treatment is continued. When sodium has been completely removed, however, the charge, which is a mixture of sodium carbide, Na_2C_2 and monosodium acetylene, $NaHC_2$, is transferred through the side arm, E, into a large test-tube, which has previously been filled with acetylene. This is now heated under a vacuum, the temperature being raised by stages, as the acetylene evolution, due to decomposition of monosodium acetylene, begins to diminish, until about 200° is reached. Three or four hours are required to complete the decomposition.

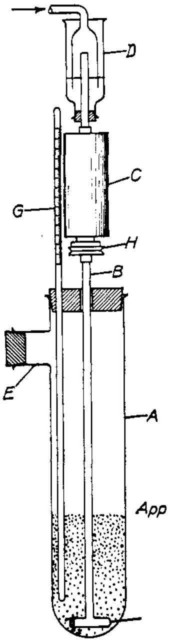

Fig. 1.—Apparatus for preparation of sodium carbide.

The sample of carbide used in the following experiments was prepared by this method and contained sodium carbide, 96.2%; monosodium acetylene, 0.4%. The remaining 3.4% of this sample was non-alkaline and appeared to consist largely of a tarry substance which may be sup-

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

posed to have been formed by condensation of acetylene. This was the best product obtained.

Other samples prepared contained about 95% of sodium carbide.

The Phases Present in the Sodium-Carbon System.—The equilibrium system formed by heating an excess of sodium carbide in a closed container to a temperature high enough to cause appreciable dissociation contains two solid phases, sodium carbide and carbon, and a gas phase containing sodium and sodium carbide, the concentration of the carbide being, however, negligible in comparison with that of the metallic sodium at the temperatures at which the measurements to be reported were made. The nature of the condensed phase was established by heating closed iron containers filled with sodium carbide to 550°, 650° and 750°, respectively, for one hour and testing afterward for the presence of metallic sodium by means of dry liquid ammonia. It had been thought possible that at these temperatures sodium carbide might dissociate to give liquid metallic sodium or perhaps a phase containing both sodium and sodium carbide. No sodium was found, however. The carbide remained unfused at 750°.

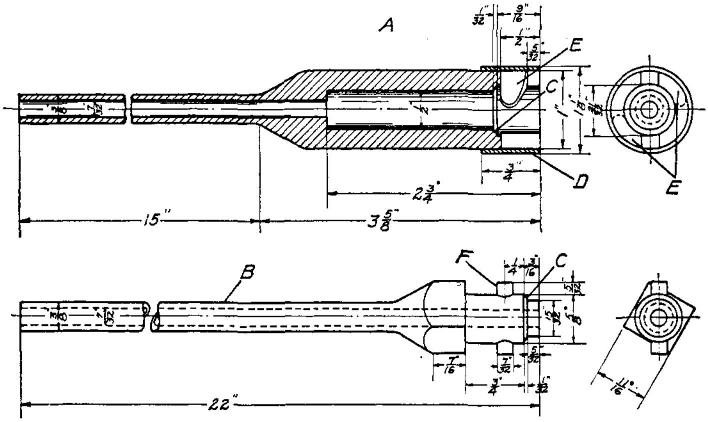

Fig. 2.—Decomposition apparatus.

The Measurement of the Dissociation Pressure of Sodium Carbide.—It appears from the above that the dissociation of solid sodium carbide is monovariant. The dissociation pressure of sodium from sodium carbide has been measured by a dynamic method at 600°, 650° and 700°. The method is as follows.

The chamber A (see Fig. 2) is filled with sodium carbide, pads of steel wool at either end serving to hold this powdery material in place. The "condenser" tube B is then attached by turning the pins F, in the helical groove E so that a gas-tight connection is made by the seat C. This apparatus is constructed of Monel metal. After the apparatus has been filled with hydrogen, heat is applied by means of an electric tube furnace of the split type, the end of B being shut off during the elevation of the temperature, so that the expansion of gas carrying some sodium from decomposition is in the opposite direction. The temperature is measured by a Chromel-Alumel thermocouple, the junction of which is placed adjacent to the middle portion of the chamber A and surrounded, together with the chamber, by a wrapping of asbestos paper. When the desired temperature is reached, a slow stream of hydrogen at atmospheric pressure is caused to pass through the heated sodium carbide and then through the tube B where, on account of the small flows used, all of the sodium is condensed. The flow of hydrogen was measured by an orifice meter following the dissociation apparatus and the total volume of hydrogen passed was obtained by multiplying the rate of flow by the time. In two experiments, helium was used instead of hydrogen, but the results were the same within the experimental error.

The partial pressure of sodium in the hydrogen leaving the dissociation chamber is readily calculated from the amount of sodium condensed in tube B, which is obtained by titrating the washings from this tube, and from the total volume of hydrogen passed. In the calculation of these partial pressures sodium vapor is assumed to be monatomic.[3] The apparent dissociation pressures were thus calculated from the results at three flows and the true dissociation pressure was obtained by extrapolating to zero flow. The results are shown in Table I.

Table I

The Decomposition Pressure from Solid Sodium Carbide

	Partial pressures									
	At 20 cc./min.			At 10 cc./min.			At 5 cc./min.			
Temp. °C.	No. of expts.	Av. part. pres.	Av. % variation	No. of expts.	Av. part. pres.	Av. % variation	No. of expts.	Av. part. pres.	Av. % variation	Extrapolated at zero flow
600	3	15	4	3	22	17	11	28	11	32
650	3	65	6	3	71	3	11	75	8	79
700	3	144	3	4	167	15	16	179	5	191

Since this decomposition is monovariant, the dissociation pressure is related to the heat Q, of the reaction

$$\underset{\text{Solid}}{Na_2C_2} = \underset{\text{Gas}}{2Na} + 2C \qquad (1)$$

by Equation 2, assuming that sodium vapor obeys the perfect gas laws.

$$\frac{d\, ln\, P_{Na}}{dt} = \frac{1}{2}\frac{-Q}{RT^2} \qquad (2)$$

Assuming as a first approximation that Q is constant from 600° to 700°, this equation becomes when integrated,

$$ln\,\frac{P_2}{P_1} = \frac{-Q(T_2 - T_1)}{2 \times RT_1T_2} \qquad (3)$$

Using the values for P_2/P_1 obtained from the measurements at 600–650° and 650–700°, respectively, the values for Q are —57,700 and —62,700

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[3] Scott, *Wied. Ann. Beibl.*, **12**, 411 (1881). Wenz, *Ann. Phys.*, **35**, 951 (1910).

calories, an average of —60,200 calories. This is made up of the heat of dissociation of solid sodium carbide to solid sodium and carbon, which is +9800 at ordinary temperature, and of the heat of fusion (which is small enough to neglect) and vaporization of two gram molecules of sodium. Assuming that the heat of dissociation of sodium carbide to solid sodium and carbon is constant between 600° and 700°, it may be seen that the heat of vaporization of sodium must be —70,000 calories for 2 Na or —35,000 calories per gram atom if the net heat of the dissociation to give gaseous sodium is to be 60,200 calories. This appears high, since it may be roughly estimated by Trouton's rule that the heat of vaporization should be about —21,000 calories. There are, however, no data available from which this heat of evaporation may be calculated and it will, therefore, be necessary to use the above value for Q, —60,200 calories, in estimating the course of the decomposition pressure curve at temperatures higher than those at which these measurements were made. Equation 3, therefore, becomes

$$ln \frac{P_2}{P_1} = \frac{30,100\ (T_2 - T_1)}{R\ T_1T_2} \qquad (4)$$

or, assuming the dissociation pressure found for 650° to be correct, this equation reduces to

$$\log p = 9059 - 6609/T \qquad (5)$$

Values of p as calculated from this equation are plotted against the temperature in Fig. 3. This equation gives 185 for the dissociation pressure at 700 instead of 191, as found. This discrepancy of 6 mm. corresponds to about 2° error in the measurement of the temperature and the temperature control was hardly as close as that. According to the curve, the dissociation pressure becomes 760 mm. at 797°. This dissociation temperature was roughly checked in a more direct manner by heating to various temperatures a small iron cylinder containing sodium carbide, with the ends loosely closed and noting the temperature at which the loss of sodium from the container began to be considerable. These experiments indicated that the dissociation temperature is between 800° and 825°. At 825° the decomposition of the carbide was found to be complete even when a mixture of sodium carbonate and sodium cyanide was added with the sodium carbide, showing that sodium carbide is not sufficiently soluble in a sodium carbonate-cyanide melt to increase its thermal stability appreciably. This point is of interest in connection with the fixation of nitrogen by a heated mixture of sodium carbonate, carbon and iron during which such a carbonate-cyanide melt is, of course, present. It appears from these experiments that sodium carbide can exist only in the gas phase in the system sodium carbonate-carbon-iron-nitrogen, during the formation of cyanide for which a temperature of 900–1000° is used.

Approximate Determination of the Dissociation of Sodium Carbide in the Gas Phase.—It was next sought to determine the gas phase equilibrium between sodium carbide and sodium at 700° by determining the amount of sodium carbide as well as total sodium in the condenser tube B. In two experiments, therefore, moist air was drawn through the detached condenser tube and then into silver nitrate solution. The nitric acid liberated according to the reaction $2AgNO_3 + C_2H_2 = 2HNO_3 + Ag_2C_2$ was then titrated. The vapor pressure of sodium carbide calculated from these two experiments was only 0.64 mm. and 0.59 mm., respectively, as compared with a dissociation pressure of sodium of 191 mm. These determinations, while not highly accurate, were sufficient to show that at 700° sodium carbide is largely dissociated in the gas phase. It is to be expected that the carbide will become more stable with increasing temperature, due to its endothermic character. Evidence has, in fact, been obtained that at 900–1000° the carbide is dissociated to a much less degree than at 700°. Definite values for the equilibrium constant for this dissociation at the higher temperatures cannot now be given, however.

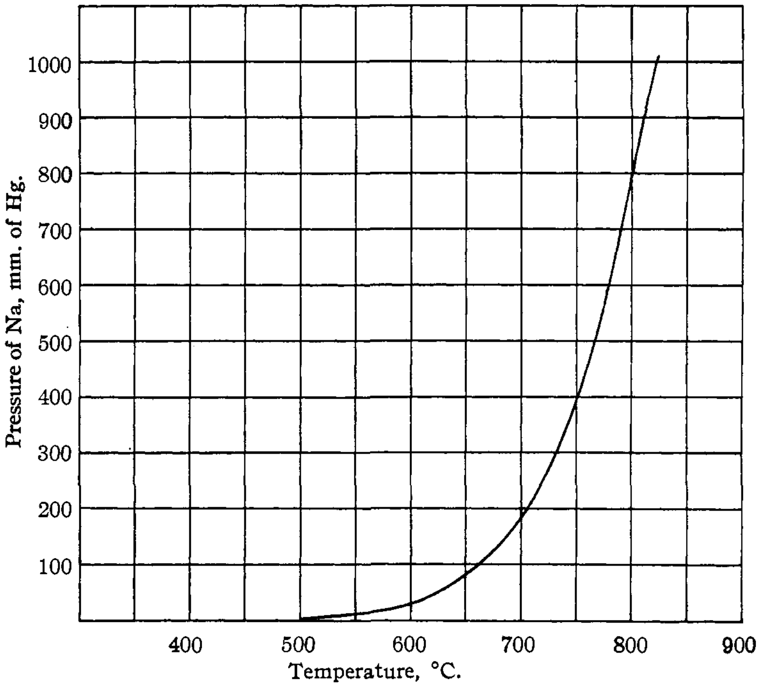

Fig. 3.—Decomposition pressure of sodium carbide. ($\log P = 9.059 - 6.609/T$.)

Summary

1. An apparatus and technique for the preparation of sodium carbide from acetylene and molten metallic sodium are described.

2. The dissociation pressure of sodium vapor from solid sodium carbide is represented approximately by the equation: $\log p = 9059 - 6609/T$.

3. The dissociation pressure becomes one atmosphere at about 800°. It follows that any sodium carbide which is formed as a step in the fixation of nitrogen as cyanide can exist only in the gas phase, since considerably higher temperatures are required for the fixation.

4. At 700°, sodium carbide in the gas phase is largely dissociated, the partial pressure of gaseous sodium carbide over solid sodium carbide being about 0.6 mm. of mercury as compared with 191 mm. dissociation pressure of sodium.

WASHINGTON, D. C.

THE POLYSULFIDES AND POLYSELENIDES OF LITHIUM, SODIUM AND POTASSIUM

BY F. W. BERGSTROM[1]

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Introduction

In connection with an investigation of the action of liquid ammonia solutions of the alkali metal amides—bases of the ammonia system—upon elements more electronegative than cobalt or nickel, it was necessary to study the action of solutions of the alkali metals upon sulfur and selenium, previous work of Hugot along these lines having been found inaccurate in many details.[2]

Procedure and Preparation of Materials

The solubility of sulfur and selenium in solutions of the alkali metals was determined essentially according to the method of Kraus and Chiu.[3] Briefly a weighed stick of sulfur or selenium was suspended in a liquid ammonia solution containing a known weight of alkali metal at —33°. At the end of the stages of the reaction corresponding to the disappearance of the blue color of the alkali metal solution, to the disappearance of a precipitate, or at the point corresponding to the saturation of the solution with respect to the more electronegative element, the stick was raised, washed with liquid ammonia and weighed. The volume of the solution was determined with sufficient accuracy from graduations on the bulb of the reaction tube.

Weighed quantities of sodium and potassium were enclosed in glass capsules according to the method of Kraus and Chiu.[3] Lithium, as it could not be melted into capsules of the glass on hand, was weighed rapidly from a weighing bottle. Sulfur, a special preparation of Kahlbaum, was

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[1] National Research Fellow.

[2] Hugot, *Compt. rend.*, **129**, 299 (1899).

[3] Kraus and Chiu, THIS JOURNAL, **44**, 2002 (1922).