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The Radioactivation Analysis of Semiconductor Graphite for Nitrogen by the $^{14}N(p, \alpha)^{11}C$ Reaction

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The excitation curve for the $^{14}N(p, \alpha)^{11}C$ reaction was measured up to a proton energy of 15 MeV.; the reaction was found to have a fairly high cross section for a sensitive determination of nitrogen by radioactivation. A convenient technique was developed for the rapid quantitative conversion of the irradiated graphite into carbonate within a closed system. This technique makes possible the determination of a trace (down to several p.p.b.) of nitrogen in pyrolytic graphite. Discussions of the possible interference (i. e., that of boron by the $^{11}B(p, n)^{11}C$ reaction) will also be given. The nitrogen content of the pyrolytic graphite sample was found to vary markedly according to the starting material and to the preparation conditions.

The development of reliable methods for determining an ultra-trace quantity of nitrogen has been required because of its ultimate importance in the physicochemical study of hyper-pure substances, especially of semiconductor materials. Previously, we reported, in a short communication,[1] that radioactivation analysis by means of the $^{14}N(p, \alpha)^{11}C$ reaction is useful for determining a trace quantity of nitrogen in pyrolytic graphite for semiconductors. In this paper, the excitation curve for the $^{14}N(p, \alpha)^{11}C$ reaction, a detailed description of the chemical process, and some results of the determination will be given, along with a discussion of the possible interferences.

Pyrolytic graphite is prepared by the thermal decomposition of an organic vapor, the carbon from the organic substance depositing onto a heated substrate to give gradually a crystalline, lustrous plate with profitable semiconductor characteristics. The pyrolytic graphite prepared from pyridine was found to have fascinating semiconductor properties.[2] The presence of a trace quantity of nitrogen is considered to give it these properties.

As is shown in Table I, all previously-reported methods are unsatisfactory for determining a trace of nitrogen in graphite; they are either inapplicable to the matrix or are of insufficient sensitivity. Further, since nitrogen is abundant in air, the sample surface, the analytical reagents and apparatus are always contaminated with it. The present method is of a very high sensitivity (a few p.p.b. of nitrogen) and is free from the contamination effect. Further, because of its extreme thermal stability, pyrolytic graphite is a suitable matrix to be analyzed by charged-particle activation; a sample with less thermal stability is apt to melt or decompose during the irradiation.

A chemical process involving a rapid quantitative decomposition of the irradiated graphite is necessary, as will be explained later. Since pyrolytic graphite is quite resistant to chemical attack, some ingenuity is required for the decomposition. The technique described in this paper is not only suitable for the present purpose, but is useful also for the rapid quantitative decomposition of many kinds of substances within a closed system.

The Excitation Curve for the $^{14}N(p, \alpha)^{11}C$ Reaction, and a Discussion of Possible Interferences

The excitation curve for the $^{14}N(p, \alpha)^{11}C$ reaction up to 15 MeV. was measured by the stacked-foil method; the results are given in Fig. 1. Because of the possible error involved in the proton-beam monitoring and in the absolute activity measurements, the absolute value of the cross section is less certain than the shape of the excitation curve, although the uncertainty must be within 20%. The mean recoil range of the ^{11}C produced by 14.2 MeV. protons was also measured by inserting a recoil catcher in the stack; it was found to be 0.36 mg./cm².

The irradiation of carbon itself with 15 MeV.

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[1] T. Nozaki and K. Yazawa, This Bulletin, **37**, 1891 (1964).

[2] K. Takeya, Y. Yazawa, N. Okuyama and H. Akutsu, *Phys. Rev. Letters*, **15**, 111 (1965).

TABLE I. ANALYTICAL METHODS FOR TRACE NITROGEN

Method	Detection limit*	Application to graphite	Removal of surface contamination	Interference etc.
Vacuum fusion	~1 p. p. m.	×	×	
Kjeldahl	>1 p. p. m.	×	×	Contamination from reagents
Emission spectroscopy	~10 p. p. m.	○	△	Contamination by residual air
Mass spectroscopy	~10 p. p. b.	△	×	
Radio-activation analysis $^{14}N(n, 2n)^{13}N$ $^{14}N(\gamma, n)^{13}N$	a few p. p. m.	○	○	Difficulty in the chemical separation of nitrogen
$^{14}N(p, \alpha)^{11}C$	several p. p. b.	○	○	$^{11}B(p, n)^{11}C$

○: Suitable, △: Difficult, ×: Impracticable
* For a convenient matrix.

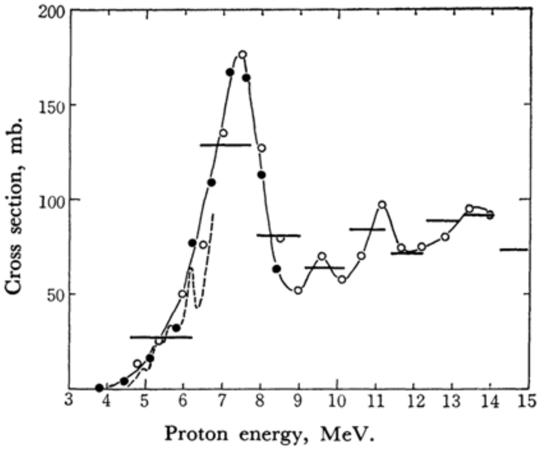

Fig. 1. The excitation curve for the $^{14}N(p, \alpha)^{11}C$ reaction.
Full line: Our result (—: nylon;
○, ●: aluminum nitride)
Broken line: Blaser's result[13]

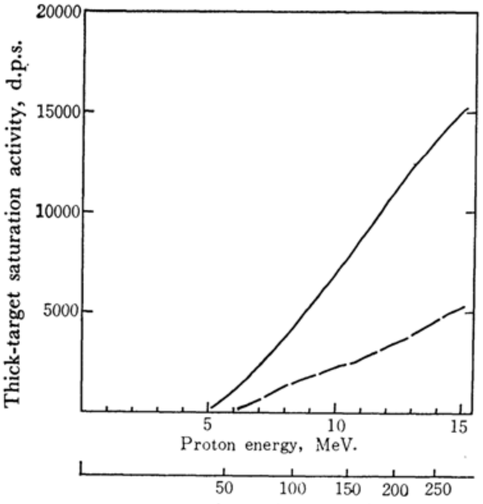

Fig. 2. The thick-target saturation activity of ^{11}C. (see text)
—— $^{11}B(p, n)^{11}C$
— — $^{14}N(p, \alpha)^{11}C$

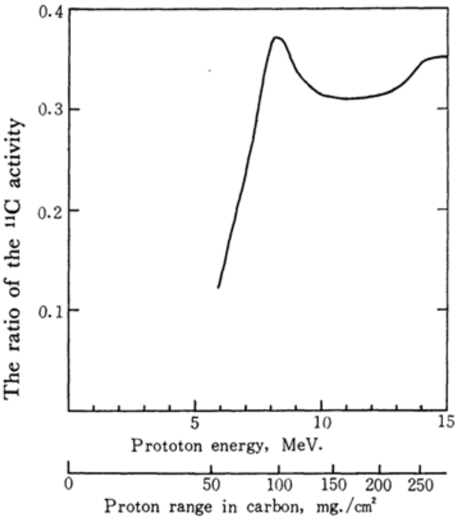

Fig. 3. The ratio of the ^{11}C activity formed from nitrogen to that from boron. (see text)

protons gives no ^{11}C, since the threshold for the $^{12}C(p, pn)^{11}C$ reaction is 20.2 MeV. There is, however, another reaction, namely, $^{11}B(p, n)^{11}C$, which gives ^{11}C on the proton irradiation.[3] Figure 2 shows the thick-target saturation activity of ^{11}C produced by irradiating carbon containing 1 p.p.m. (by weight) of nitrogen or of boron (natural isotopic composition) with a 1 μamp. proton beam. Figure 3 shows the ratio of the ^{11}C activity formed from nitrogen to that formed from boron, when a thick matrix containing equal amounts (weight fraction) of the two elements is irradiated with protons. The thick-target yield varies with the nature (the stopping power) of the matrix, but the ratio is almost independent of it.

As is evident from Fig. 2 and Fig. 3, in the presence of boron nitrogen cannot be determined by proton activation in a single irradiation. Alternately, two irradiations at different proton energies, followed by the solution of the pair of simultaneous equations thus obtained, do not seem to

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[3] M. Furukawa, Y. Ishizaki, Y. Nakano, T. Nozaki, Y. Saji and S. Tanaka, *J. Phys. Soc. Japan*, **15**, 2167 (1960).

give accurate results. By radioactivation analysis using the $^{10}B(d, n)^{11}C$ reaction, an ultra-trace quantity of boron can be determined in the presence of nitrogen. However, this method is not suitable for the graphite matrix because of the simultaneous formation of a very high activity of ^{13}N due to the $^{12}C(d, n)^{13}N$ reaction.

Fortunately, however, the determination of a trace of boron in graphite has been well studied because of its importance in nuclear engineering. Both direct spectrography(4) and spectrography or spectrophotometry after ashing the sample in the presence of calcium oxide or lanthanum oxide(5,6) are useful. In the latter process, the methods developed for determining an ultra-trace quantity of boron in transistor-grade silicon(7) or in germanium are also applicable with slight modifications. Hence, it appears preferable to determine boron by one of the above method prior to the proton activation.

It was certain, however, that most of our present samples contained much less boron than nitrogen, because they were prepared from pyridine. Hence, without the prior determination of boron, their nitrogen content could be determined reliably.

The Elimination of the Surface Contamination

Surface contamination is easily eliminated by removing a surface layer of a suitable, uniform thickness after the irradiation. The layer thickness depends on the recoil range of the radio-nuclide and on the roughness of the initial surface. It has been shown previously that a surface layer of about 5 times the thickness corresponding to the recoil range should be removed.(8) Hence, for the present case, a surface layer about 1.8 mg./cm^2 thick should be removed. However, since the uniform removal of such a thin surface is difficult and since the initial surface roughness is not precisely known, it is considered preferable to grind off a surface layer of a greater thickness (5 to 10 mg./cm^2).

Chemical Process

The nuclide ^{11}C has a 20.4 min. half-life and emits positrons but no γ-rays. The proton irradiation of carbon gives a high activity of ^{13}N by the $^{13}C(p, n)^{13}N$ reaction,(9) the abundance of ^{13}C being 1.1%. ^{13}N also emits positrons and has a 10.0 min. half-life. Many kinds of impurities also give positron emitters on proton irradiation. Therefore, a trance of nitrogen in graphite cannot be determined by nondestructive γ-ray spectrometry; a chemical purification of the ^{11}C involving a rapid decomposition of the sample is required. In the purification, the matrix graphite itself is the carrier of ^{11}C.

After the irradiation with charged particles, the radionuclide formed is not distributed uniformly in the sample, and the radiation effect might have changed the chemical reactivity of the irradiated portion. Therefore, a quantitative treatment of the pyrolytic graphite involving its oxidation under drastic conditions is required until a homogeneous phase containing all of the carbon is obtained.

Wet oxidation in a mixture of sulfuric and condensed polyphosphoric acid provided a useful method of decomposing the sample. Kiba and his associates(10) describe the stoichiometrical oxidation of charcoals and naturally-occurring graphite with potassium iodate in condensed polyphosphoric acid. For the present purpose, the technique they described should, however, be slightly modified, because pyrolytic graphite is more resistive to oxidation than charcoals and graphites of other sources, and because a larger quantity (up to 1 g.) of the sample should be oxidized. The following modifications proved to be convenient: (1) a mixture of sulfuric and condensed polyphosphoric acid was used as the oxidation medium(11); (2) a small quantity of perchloric acid was added near the end of the oxidation; and (3) the reaction temperature was raised slowly but continuously in the course of the reaction. Without these modifications, the oxidation was often incomplete with the formation of the so-called graphitic acid, which was still less oxidizable than the graphite itself. The fine pulverization of the sample with the aid of added alumina or silica(10) was of ultimate importance for the smooth oxidation. The perchloric acid, oxidizing the deep-colored molecular iodine formed in the reaction, was effective also in facilitating the observation of the reaction from outside.

The equipment shown in Fig. 4 was devised for oxidizing the graphite and absorbing quantitatively the carbon dioxide formed to yield a homogeneous phase. The oxidation and the absorption were carried out in a closed system. The absorbed carbon dioxide was further purified, because it probably contained such radiochemical impurities as were distilled from an oxidizing medium.

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4) E. g. F. W. J. Garton, *Spectrochem. Acta,* **9**, 297 (1957).

5) E. g. T. Nakajima, M. Takahashi and M. Morishita, *J. Atom. Energy Soc. Japan,* **3**, 104 (1961).

6) E. g. T. Takeuchi, M. Suzuki and Y. Miwa, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi),* **64**, 1367 (1961).

7) E. g. G. H. Morrison and R. L. Rupp, *Anal. Chem.,* **29**, 892 (1957).

8) K. Saito, T. Nozaki, M. Furukawa, S. Tanaka and H. Cheng, *Intern. J. Appl. Radiation Isotopes,* **14**, 358 (1963).

9) A. B. Whitehead, *Can. J. Phys.,* **36**, 1283 (1958).

10) T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Japan Analyst,* **2**, 446 (1953).

11) M. Ura, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi),* **78**, 316 (1957).

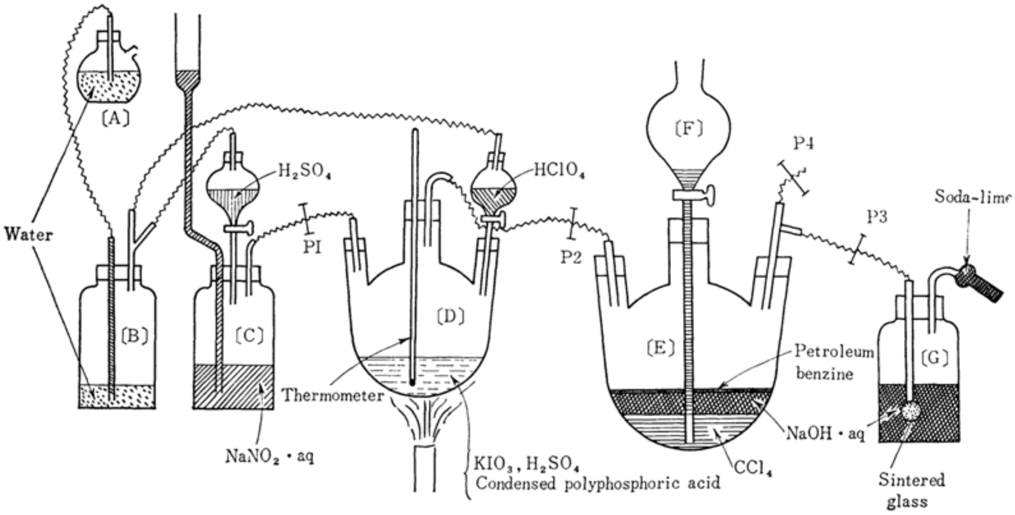

Fig. 4. Equipment for the chemical process.
P: Pinch-cock; 〰 : Rubber tube

It was then converted into barium carbonate for activity and recovery measurements. The details concerning the operation of the equipment are given in the Experimental Section.

It took 40 to 50 min. for the barium carbonate to be obtained after the irradiation. Its radiochemical purity was so high that a satisfactory decay curve was obtained by measuring the annihilation radiation with a simple scintillation counter.

The Calculation of the Nitrogen Content

For a sample of a given nitrogen content (e. g., 1 p. p. m.), the absolute ^{11}C-activity induced in it can be calculated by the use of the integral excitation curve (Fig. 2) when the sample thickness, the initial proton energy, the proton-beam current, and the irradiation duration are known. Also, the absolute ^{11}C-activity contained in the analyzed sample (at the end of the irradiation) can be calculated by the use of the measured activity and recovery and of the counting efficiency. The above two calculations were made for each sample, and its nitrogen content was obtained from the resultant values.

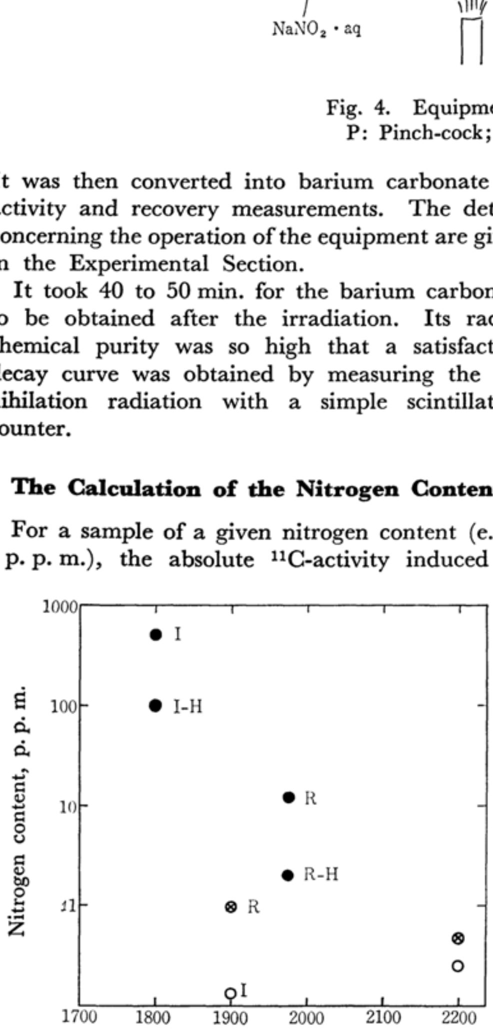

Fig. 5. Nitrogen content of the pyrolytic graphite.
●: Prepared from pyridine ; ○: Prepared from propane; ⊗: Prepared from propane in nitrogen atmosphere.
I : By induction heating ; R : By resistance heating ; —H: Heat-treated.

The Results of the Analysis

Some of the analytical results are given in Fig. 5. Figure 6 shows the decrease in nitrogen content on heat treatment, in which samples prepared from pyridine at 2150°C were kept at 2300°C in a nitrogen atmosphere (ca. 10 cmHg). Although the interference of boron should be taken into account for the sample with a low nitrogen content, the following facts can be derived unambiguously:

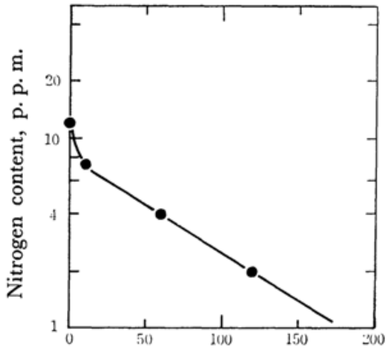

Fig. 6. Escape of the nitrogen on heat treatment.

(1) the sample from pyridine contains much more nitrogen than that from propane; (2) the presence of nitrogen gas in the preparation of pyrolytic graphite from propane does not make the nitrogen concentration in the product markedly higher; (3) the nitrogen concentration in the sample from pyridine depends on the temperature of the preparation—the higher the temperature, the lower the content; and (4) when the sample from pyridine is heated, the nitrogen content decreases.

Experimental

The Measurement of the Excitation Curve.—Nylon films of a known thickness (ca. 20 mg./cm^2) with thin aluminum foils (also of a known thickness) on both sides of each film were stacked. The stack was bombarded with a proton beam (15 MeV., 0.1 μamp.) from the cyclotron of the Institute for Nuclear Study, The University of Tokyo, for 1 min., the integrated beam current being read by an integrator. Each of the nylon films with the aluminum foils was sandwiched between bronze plates (ca. 3 mm. thick) for counting. The annihilation radiation from each sandwich was measured by a scintillation counter with a single channel analyzer, whose counting efficiency was calibrated with a standard ^{22}Na source. By following the decay, the sample activity was found to consist only of ^{11}C and ^{13}N. Thus, after the analysis of decay curve, the cross section of the ^{14}N(p, α)^{11}C reaction was calculated for each of the films.

The energy loss[12] (in MeV.·cm^2/g.) of charged particles in a compound is regarded as the sum of that in each element making up the compound in proportion to its weight fraction (the additivity rule). However, when the proton energy at each of the nylon films was calculated by the use of the additivity rule, an unreasonable result was obtained: the reaction appeared to have a considerably large cross section for proton energies below its threshold. There are two possible explanations of this result: (1) an incorrectness in the additivity rule for compounds consisting of light elements, especially for those containing hydrogen, or (2) a change in the thickness of the films in the course of the irradiation. No apparent thickness change, however, was observed in the irradiated part of the film. Hence, the value given by the additivity rule was slightly modified and used for the present calculations.

A more reliable experiment was undertaken by the use of a stack consisting of aluminum nitride films and aluminum foils. Fine powder of aluminum nitride was suspended in acetone, and allowed to deposit onto an aluminum foil of a known thickness to form a uniform film with the aid of a small, known quantity of polyvinyl acetate as a binder. The thickness of film was determined from its weight and area. Two stacks were bombarded with proton beams of different initial energies. The excitation curves obtained by the use of the stack material and of the additivity rule for the proton energy loss are of a reasonable form, agreeing with Blaser's result in the low-energy region.[13]

The Preparation of the Pyrolytic Graphite.—In a stream of propane or pyridine vapor (4 to 7 mmHg), a substrate plate was heated (1800 to 2200°C) by direct current (resistance heating) or by induction. The pyrolytic graphite grew at a rate of 50 to 300 μ/hr. The sample preparation from propane was also carried out in the presence of nitrogen (6 to 10 mmHg).

Irradiation, and the Removal of the Surface Contamination.—A rectangular window (10 mm. × 20 mm.) was cut in a metal plate thick enough to stop the protons. A graphite plate (0.4 to 2.0 mm. thick) slightly larger than the window was placed between a water-cooled target holder and the window of the metal plate, well in contact with both. It was then irradiated with a deflected proton beam (14 MeV., 10 μamp., 10 min.), the beam current being recorded. Since a part of the beam impinged on the metal plate at the edges of the window, the activity induced in it was measured and compared with that obtained on irradiating the metal plate without a window under the same conditions. Thus, the beam flux received by the sample itself was determined.

The sample surface was removed as uniformly as possible by grinding on a flat plate with the aid of fine alundum powder (both sides for a thin sample, one side for a thick sample). The thickness of the surface layer removed was determined by measuring the surface area and the loss of weight. The sample was then pulverized in a tall iron mortar in the presence of alumina powder (ca. 1 g.).

The Chemical Process.—In Fig. 4, A and B were for supplying a suitable pressure, while C was for generating nitrous fumes (gas formed on treating sodium nitrite with sulfuric acid).

Condensed polyphosphoric acid convenient for the present purpose was prepared by heating orthophosphoric acid up to 300°C during 40 min. and keeping it at 300°C for 20 min. The condensed polyphosphoric acid (50 ml.), sulfuric acid (35 ml.) and potassium iodate (25 g.) were added into D (500-ml. three-necked flask), and the mixture was heated gently. Into E (1-l. three-necked flask) were added carbon tetrachloride (300 ml.), carbonate-free sodium hydroxide solution (1.5 N, 200 ml.), and petroleum benzine (a few milliliters) to form three layers. When the temperature of the mixture in D reached 160°C, the air in D and E was replaced by nitrous fumes streaming from P1 to P4. After P1 and P4 had been closed, the stopper of the central neck of D was momentarily opened, and the pulverized sample was quantitatively added through the neck. Gentle heating was continued.

When oxidation began, a part of the carbon tetrachloride was pushed into F. Then E was shaken from outside to remove the petroleum benzine layer by being absorbed in the carbon tetrachloride beneath the sodium hydroxide solution. When the evolution of carbon dioxide became feeble even at 230°C, perchloric acid (60%; less than a few milliliters) was carefully dripped into D. A gentle shaking of D and E was necessary throughout to cause the oxidation process to proceed smoothly. When all of the sample had been oxidized, P1 was opened and the carbon dioxide remaining in D was carried into E with nitrous fumes.

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[12] R. M. Sternheimer, *Phys. Rev.*, **115**, 137 (1959).

[13] J. P. Blaser, P. Marmier and M. Sempert, *Helv. Phys. Acta*, **25**, 442 (1952).

Without A and B, neither the sulfuric acid not the perchloric acid could be added smoothly. Without the replacement of air by nitrous fumes, the air expelled most of the sodium hydroxide solution into F before the carbon dioxide came into E. The nitrous fumes also served as a hold-back carrier for ^{13}N. Without the benzine layer, nitrous fumes were freely absorbed by the sodium hydroxide before the commencement of oxidation, and air entered E from F. The determination of the carbonate in E proved that the quantitative conversion of the graphite sample into the carbonate had taken place.

Hydrazine hydrate (60%; 20 ml.) and hydrochloric acid (2 N; 200 ml.) were successively added to E from F, with P3 open and P2 closed. The carbon dioxide thus evolved was caught by carbonate-free sodium hydroxide solution (1.5 N; 100 ml.) in G. The heat of neutralization evolved in E effectively caused the carbon dioxide to be forced into G, the vapor of benzine and carbon tetrachloride filling the vacancy in E. The solution in G was added to a hot solution of barium chloride (0.5 N, an amount equivalent to the sample carbon), and the barium carbonate was filtered off with suction and washed with hot water. The recovery of the sample carbon was determined gravimetrically after the activity measurement.

The Activity Measurement.—The annihilation radiation of ^{11}C in the barium carbonate was measured by a calibrated scintillation counter with a single channel analyzer. The decay of the barium carbonate activity was followed to ascertain the radiochemical purity. Also, the γ-ray spectra of some of the barium carbonate samples were measured by a multi-channel analyzer to ascertain the absence of γ-rays other than the annihilation radiation.

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