Thermal Neutron Capture Cross Section of Carbon-13

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The thermal neutron capture cross section of C^{13} has been determined from the amount of C^{14} formed in pile-irradiated samples of graphite, barium carbonate, and carbon dioxide. Because of the impurity reaction, $N^{14}(n,p)C^{14}$, of comparatively high cross section, the results were consistent only when samples were used which were enriched in C^{13}.

The average isotopic cross section determined for the enriched samples was 1.4 ± 0.2 millibarns. The final value of the cross section in these samples corrected for the estimated residual nitrogen impurity is 0.9 ± 0.2 millibarn.

INTRODUCTION

THE total cross section of carbon for the capture of thermal neutrons has been reported[1] as 4.5 to 4.9 millibarns. The method used to determine this value does not distinguish between C^{12}, C^{13}, or residual absorption. The present investigation has been carried out to determine the extent to which this cross section is due to neutron capture by C^{13}.[2] The method entailed the irradiation of carbon-containing samples with moderated pile neutrons and the radiochemical determination of the yield of C^{14}. Extreme care was necessary to minimize the spurious production of C^{14} from nitrogen impurities by the reaction $N^{14}(n,p)C^{14}$. To ascertain the most favorable conditions for reducing this nitrogen contamination, the carbon was irradiated in several chemical forms such as graphite, barium carbonate, and carbon dioxide. Furthermore, samples were prepared in which the C^{13} isotopic concentration had been artificially enhanced to increase the yield of C^{14}. These enriched samples had to be analyzed for C^{14} even before irradiation since C^{14} is present in many natural sources of carbon dioxide and becomes concentrated even more than C^{13} during the isotope enrichment process.[3]

The samples were irradiated in the Argonne CP-3 heavy water moderated pile. The slow neutron flux was estimated in most cases by placing lead nitrate samples adjacent to the carbon samples during irradiation and determining the C^{14} produced from the nitrogen in these monitors.

[1] National Bureau of Standards Nuclear Data Group, Natl. Bur. Standards (U. S.) Circ. No. 499 (U. S. Government Printing Office, Washington, D. C., 1950).

[2] In a recent compilation of cross sections [D. J. Hughes *et al.*, U. S. Atomic Energy Commission Report AECU-2040 (Technical Information Service, Department of Commerce, Washington, D. C., 1952).], a value of 1.0 ± 0.3 mb was included for the cross section of C^{13}. It is believed that this compilation quoted the results of the determination discussed herein. This value was reported by the author in an Argonne National Laboratory Report ANL-4345, October 11, 1949 (unpublished). The difference between the earlier value of 1.0 ± 0.3 mb and the 0.9 ± 0.2 mb value reported in the present paper is due merely to the use of a more proper method of weighting the individual determinations.

[3] Anderson, Libby, Weinhouse, Reid, Kirschenbaum, and Grosse, Science **105**, 576 (1947).

EXPERIMENTAL PROCEDURES

Sample Preparation

High-purity graphite was heated in quartz tubes to 1000°C for times up to 24 hours. The samples were evacuated during this heat treatment, and were sealed into the same quartz tubes after cooling.

Samples of a $BaO-BaCO_3$ mixture were prepared from Baker analyzed barium oxide which had been degassed in quartz tubes for three hours at 900°C in vacuo. This material was reacted with twice-sublimed carbon dioxide at 400°C for 24 hours.

Barium carbonate was prepared by reacting twice-sublimed carbon dioxide with boiled, filtered barium hydroxide solution. The precipitation of barium carbonate was carried out in the absence of air, and the filtration was carried out in an atmosphere of helium. The filtered barium carbonate was dried in air at 120°C, then *in vacuo* at 500°C, and finally sealed in evacuated quartz tubes.

Carbon dioxide was sublimed several times for purification, and irradiated in long quartz tubes at nearly atmospheric pressure. The quartz tubes were pretreated by heating in air at 1000°C, and heating further after evacuation. They were provided with break-off seals at one end to facilitate removal of the gas after irradiation.

Lead nitrate was recrystallized twice. Weighed samples were placed in quartz tubes of less than 4-mm inside diameter (to insure uniformity of flux), evacuated, and sealed off.

Sample Processing

After irradiation, the quartz capsules containing solid samples were boiled in alkaline permanganate and aqua regia to remove externally deposited C^{14} and placed in a breaking device which permitted fracturing the capsules in an evacuated container. For carbonate samples, the broken fragments of the quartz tube and its contents were allowed to drop into the bottom of the breaking device which contained concentrated sulfuric acid. Reaction with the acid released carbon dioxide. For the lead nitrate samples, water and carrier carbon dioxide had been frozen into the breaking device.

On warming, these samples dissolved in the water and released C^{14} as carbon dioxide.

Graphite samples were sometimes opened in the same breaking device and burned directly in it, but this procedure was found unnecessary. Usually, the graphite samples were opened in air and transferred rapidly to a combustion tube. They were burned in oxygen and the combustion gases passed over copper oxide and lead chromate at 600°C.

Samples irradiated as carbon dioxide were frozen in their quartz container after irradiation, the container was sealed to a vacuum line and opened via the break-off seal. A small amount of carbon monoxide was added to the sample and the gases separated into carbon monoxide and carbon dioxide. It had been anticipated that some of the C^{14} formed would show up as carbon monoxide rather than carbon dioxide. A separation was accomplished by passing the gas through two traps cooled with liquid nitrogen, each containing sintered glass disks. Carbon dioxide was thus removed and remained in the traps. The carbon monoxide was then passed over hot copper oxide and the resulting carbon dioxide was condensed in a third trap. Finally the empty

Table I. C^{13} cross section determined from a BaO—BaCO₃ sample.

Sample	Fraction C¹³ in carbon	Total times con-verted	Integral neutron flux a (10¹⁷ nvt)	Count rate (cpm/150 mm)	σe (cm²)	σi (cm²)
D-17	0.4532	1	0	297±5		
		2	4.94	860±7		
		3		854±6	2.06×10⁻²⁹	1.88×10⁻²⁷

a Estimated from pile power.

quartz tube in which the sample had been irradiated was filled with oxygen and carrier carbon dioxide and heated at 1000°C to oxidize substances, presumably C_3O_2 polymers, which had formed on the wall. This fraction is labeled "C_3O_2 (wall)" in Table III.

All the carbon dioxide samples obtained in this way except the flux monitors had to be converted to methane for counting. This was accomplished by adding an excess of hydrogen and cycling over a ruthenium catalyst.[4] The catalytic reduction is fairly rapid at 350°C but requires small amounts of moisture in the reacting gas mixture. After complete reduction, the methane was separated from excess hydrogen by palladium or by copper oxide at 400°C and dried. The methane was then condensed with liquid nitrogen and purified further by pumping from the trap in which it was condensed at −196°C. The methane obtained in this way was nearly always found to contain radioactive impurities. This was established by counting the methane, and subsequently reoxidizing it to carbon dioxide over copper oxide at 900°C, drying the carbon dioxide and reducing it again. Such a reconversion cycle nearly always reduced the counting rate of the methane. The

[4] G. R. Hennig, Argonne National Laboratory Report ANL-4080, January, 1948 (unpublished).

Table II. C^{13} cross section determined from several BaCO₃ samples.

Sample	Fraction C¹³ in carbon	Total times con-verted	Integral neutron flux (10¹⁷ nvt)	Count rate (cpm/150 mm)	σe (10⁻²⁹ cm²)	σi (10⁻²⁷ cm²)
D-1	0.011	1	4.69	176±2	28.4	25.8
D-21	0.011	1	7.15	1715±16		
		2		719±11		
		3		240±9	25.5	23.2
D-24	0.011	1	5.10	386±10		
		2		119±9		
		3		107±12	16.0	14.5
D-26ᵃ	0.0622	4	6.89	392±41		
		5		354±12	6.86	6.26
D-23ᵇ	0.4532	3	0	854±6		
		4	8.52	2930±13		
		5		2000±28		
		6		1710±10	1.85	1.68
D-28	0.53	1	0	322±4		
		2	9.73	1695±12		
		3		1068±6		
		4		1029±8	1.13	1.03

a This sample had been enriched from petroleum methane, which was assumed free of C^{14} because of its age. Therefore no pre-irradiation measurements of C^{14} content was made.
b This sample had previously been irradiated as barium oxide-barium carbonate (sample D-17, Table I).

process was repeated until a constant counting rate was reached. The number of such reduction cycles for each sample are listed in Tables I to III under the heading of "times converted."

The radioactive impurity could not be eliminated by pretreating the carbon dioxide prior to reduction. Repeated passages over copper oxide and lead chromate at 600°C followed by freezing and subliming at −78°C did not eliminate the impurity. However, an efficient method for removing the spurious activity was found just in time to be adopted for the last sample examined (D-32, see Table III). The sample of carbon dioxide

Table III. C^{13} cross section determined from CO₂ samples.

Sample	Gas fraction	Fraction C¹³ in carbon	Total times con-verted	Integral neutron flux (10¹⁷ nvt)	Count rate (cpm/150 mm)	σe (10⁻²⁹ cm²)	σi (10⁻²⁷ cm²)
D-31	CO₂	0.53	2	0	322±4		
	CO₂	0.53	3	6.74	14740±10		
			4		697±11		
			5		621±3		
			6		607±6	0.66	
	CO	0.011ᵃ	1		258±7		
			2		113±6	0.26	
	C₃O₂ (wall)					(0.45)	
	Total					1.37	1.25
D-32	CO₂	0.53	2	0	322±4		
	CO₂	0.53	3	5.97	763±6		
					762±4	1.15	
	CO C₃O₂	0.011ᵃ	1		51±5	0.13	
	(wall)	0.011ᵃ	1		199±6		
			2		171±6	0.45	
			3		182±4		
	Total					1.73	1.57

a Virtually all of this sample consisted of carrier carbon of normal C^{13} abundance, and had not been converted previously.

was precipitated with barium hydroxide in the presence of small amounts of potassium permanganate. The barium carbonate formed was filtered, dried, and reacted with concentrated sulfuric acid to regenerate the carbon dioxide. This carbon dioxide did not change its counting rate on repeated reduction and reoxidation cycles.

The source of the spurious activity which was removed in this laborious procedure is still doubtful. It was probably a soft beta emitter since it did not penetrate 2 mg/cm^2 of mica. Most of the radioactive impurity followed inert gases when they were added as carriers to the carbon dioxide and subsequently separated by freezing the carbon dioxide. The amount of contaminating activity increased with the size of the quartz irradiation container.

Counting Procedures[5]

Samples containing concentrations of C^{14} exceeding 10^{-7} mole per mole of carbon (e.g., flux monitors) were counted as carbon dioxide in a glass cup sealed around the window of an end-window counter. The pressure of the carbon dioxide in the counting cup did not exceed 300 mm Hg, as determined with a mercury manometer. Standardization of the apparatus was accomplished using a sample which had been accurately diluted from a mass spectrometrically analyzed sample of $C^{14}O_2$. The standardization was repeated periodically. Low concentrations of C^{14} were measured at much higher efficiency by counting as methane in internal counters. The counters, 1279 cc in volume, 23.5 inches in length, and 2 inches in diameter, were made of brass with a 0.003- inch tungsten center wire. The gas was counted at a pressure of 150 mm Hg whenever possible. A Neher-Harper quenching circuit was used. Inasmuch as the counting efficiency depended somewhat on the methane pressure and on the counting rate, appropriate correction factors were determined by standardization with a mass spectrometrically analyzed sample of C^{14}. The counting rates of the samples were of the order of and often less than the background of the heavily shielded counter. They were therefore counted for many hours or even days. The counting rate was recorded continuously to detect spuriously high counts due to atmospheric disturbances or to the proximity of sources of penetrating radiation.

Flux Determination

Carbon dioxide from the lead nitrate samples was counted in aliquot amounts. From the counting rate and the standardization of the counter, the concentration of C^{14} in the sample was calculated and was then multiplied by the number of moles of carbon dioxide, pv/RT, to obtain N, the number of moles of C^{14} formed.

[5] It should be noted that these experiments were carried out in 1948 and 1949. Therefore scintillation and other counting methods which would now be considered for these experiments were not employed.

The integral neutron flux (nvt) was calculated from the equation

$$nvt = (N \times M)/(1.78 \times 10^{-24} \times W \times 2),$$

where $M = 331.2$ is the molecular weight of the lead nitrate monitor, 1.78×10^{-24} cm^2 the cross section of nitrogen,[2] and W the weight of the monitor.

When samples D-31 and D-32 of carbon dioxide gas were irradiated, the containers were so long that the flux varied considerably along their length. In these cases small disks of aluminum were attached to the container at six-inch intervals and a lead nitrate monitor was attached to one end. The aluminum disks were counted on an end-window counter and the average of their counting rates was divided by the count rate of the disk adjacent to the monitor. This ratio multiplied by the flux detected by the monitor was used for the average flux in the sample. The monitor for sample D-32 broke prematurely and the flux for this sample was calculated by comparing the activity of the aluminum disks with the activity of the aluminum disks from sample D-31, which had been monitored.

For a number of irradiations in which no monitor was used the flux was estimated from the known pile power in kilowatt hours and from the relation, observed for a number of monitored samples, that the flux in the sample location used in CP-3 was 1.8×10^{13} neutrons/cm^2 per kw-hr with a probable error of 10 percent.

Cross-Section Calculations

The element cross section (for C^{12} and C^{13} in normal abundance), σ_e, in Tables I to III was calculated from the equation:

$$\sigma_e = \frac{C \times R \times T}{k \times nvt \times pv \times A \times e} \frac{0.011}{f},$$

where C = counts min^{-1}, R = gas constant (cc mm °K^{-1} mole^{-1}), T = temperature (°K), k = decay constant (min^{-1}), nvt = integral neutron flux (neutrons cm^{-2}), p = pressure of the counter gas (mm Hg), v = volume of counter (cc), A = Avogadro's number, e = efficiency of counting, and f = fraction of C^{13} in the carbon of the sample. Since e was determined from a sample of known C^{14} concentration, the factor e is proportional to $1/k$ and the calculated value of σ_e is independent of the decay constant of C^{14}. The isotopic cross section σ_i for C^{13} was obtained from the relationship

$$\sigma_i = \sigma_e/0.011.$$

RESULTS

Analysis of the irradiated graphite samples for C^{14} yielded results which were so inconsistent that they have not been included in the present report. However, most of the values for the isotopic cross section determined this way fell below 2.5 mb, the lowest being 1.2 mb. It is certain that the results for graphite are

high because trace amounts of nitrogen are known to remain even after graphite has been heated to 1000°C.[6]

Several $BaO - BaCO_3$ samples were prepared from carbon dioxide of normal C¹³ abundance but they are not reported here because their counting rates after irradiation and conversion to methane were very high and quite inconsistent, due to the presence of the radioactive impurity mentioned earlier. A satisfactory procedure for removal of the impurities by repeated reconversion had not been perfected at the time of this analysis. However, one enriched sample (D-17) was subjected to the purification procedure and was reconverted a sufficient number of times to reach a constant counting rate. The results of this measurement are reported in Table I.

Results obtained from barium carbonate samples are given in Table II. Analyses of enriched samples irradiated as carbon dioxide are collected in Table III. The so-called "C_3O_2 (wall)" fraction from sample D-31 was lost during reduction. As a first approximation the value for the wall fraction of sample D-32 was also used for D-31.

DISCUSSION

Inspection of Tables I to III reveals that the cross section determined from unenriched C¹³ samples varies much more than the probable error of the individual determinations. Samples highly enriched in C¹³ agree much more closely and an average cross section was calculated from them as shown in Table IV. The

TABLE IV. Average C¹³ cross section. (Samples enriched in C¹³).

| Sample | σ_e (10⁻²⁹ cm²) | (Percent) error | |
		Est. flux	Counting rate
D-17	2.06	10	2
D-23	1.85	5	2
D-28	1.13	5	2
D-31	1.37	5	11
D-32	1.73	5	14
Average	1.54		

average cross section was arrived at by weighting each determination by the inverse square of its probable error. The errors in the individual determinations are listed in the third and fourth columns. The flux determination is in error by less than 5 percent if a monitor was used, and about 10 percent if the flux was calculated from the pile power output. The errors due to counting are the sums of all pertinent errors in statistics; i.e., $D_1 + D_2 + 2D_B$, where D_1 is the standard deviation of the count before irradiation, D_2 after irradiation, and D_B the standard deviation of the background count. Combining the individual standard deviations in Table IV, one obtains a standard deviation of 2.1

[6] C. L. Mantell, *Industrial Carbon* (D. Van Nostrand Company, Inc. New York, 1946), p. 361.

TABLE V. Cross sections of enriched barium carbonate samples corrected for nitrogen impurities.

Sample	σ_e Measured (10⁻²⁹ cm²)	σ_e Nitrogen correction (10⁻²⁹ cm²)	σ_e Corrected (10⁻²⁹ cm²)	Estimated probable error (10⁻²⁹ cm²)
D-23	1.85	0.57	1.28	±0.18
D-28	1.13	0.49	0.64	±0.13
D-17	2.06	0.57	1.49	±0.27
Weighted average			0.96	±0.19

microbarns. Thus the experimental value for the contribution of the C¹³ cross section to the cross section of the element is $1.54 \pm 0.21 \times 10^{-29}$ cm².

The results for the samples irradiated as barium carbonate show that these samples contained much nitrogen. The unenriched samples of barium carbonate, D-1, D-21, and D-24, give an average carbon element cross section of $2.3 \pm 0.5 \times 10^{-28}$ cm². This is so much larger than the value obtained from enriched samples that it can probably be attributed almost entirely to nitrogen. The amount of nitrogen calculated from this cross section is $2.3 \times 10^{-28}/\sigma_N$ atoms per molecule of $BaCO_3$, where $\sigma_N = 1.78 \times 10^{-24}$ cm². This corresponds to 9.4 parts per million of nitrogen by weight. It can be assumed further that the method of preparation used always introduced approximately this amount of nitrogen into the barium carbonate. If then the contribution of this nitrogen is calculated for the enriched samples of barium carbonate, the corrected values listed in Table V are obtained.

The amount of nitrogen present in the gas samples D-30 and D-31 cannot be estimated.

CONCLUSIONS

In conclusion it can be stated that the experimental determination of the C¹³ contribution to the carbon element cross section resulted in an average value for enriched samples of $1.5 \pm 0.2 \times 10^{-29}$ cm², but that good evidence exists that the correct value is closer to $1.0 \pm 0.2 \times 10^{-29}$ cm², the average value of the corrected results on the enriched samples listed in Table V. These values correspond to a measured isotopic cross section for C¹³ of 1.4 ± 0.2 mb and to a corrected isotopic value of 0.9 ± 0.2 mb. It is thus apparent that the contribution of C¹³ to the total measured cross section of carbon is small.

ACKNOWLEDGMENT