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A Determination of the Half-Life of Carbon 14

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Experiments are described involving the counting of an analyzed and diluted sample of carbon dioxide containing C^{14} in a Geiger counter of known effective volume. The value of the half-life is found to be 5589±75 years.

INTRODUCTION

A CONSIDERABLE number of investigators have reported measurements of the C^{14} half-life, but, even excluding the earliest estimates, the values range from 4700 to 7200 years. Factors contributing to the undertaking of this research were the availability of starting material rich in C^{14},[1] and so permitting more certainty in the number of active carbon atoms, availability of the counters used, and the possible importance of the half-life for the measurement of time.[2]

The method, in general, consisted of the mass spectrometric analysis of a sample of CO_2 rich in C^{14}, the dilution of a portion of this material in a known way, and the counting of a portion of the diluted material in a Geiger counter of known effective volume.

PREPARATION, ANALYSIS, AND DILUTION OF RADIOACTIVE CARBON DIOXIDE

The carbon dioxide containing C^{14} which was counted was obtained by dilution of some rich material with ordinary CO_2. The dilution can be performed more accurately than the mass spectrometric analysis of the original material, and it is therefore desirable that the starting material be rich in C^{14} in order to decrease uncertainty in the number of active carbon atoms. The very rich sample of $BaCO_3$ described by Norris and Snell[1] seemed ideal for this purpose, and a 39.4-mg sample of this material was made available by the Oak Ridge National Laboratory.

A small vacuum system was constructed for the conversion of small amounts of barium carbonate to carbon dioxide by means of concentrated and outgassed sulfuric acid. The gas generated was passed through a dry ice trap and was then passed several times over a tube of phosphorus pentoxide. Finally the gas was condensed into an accurately known volume of about 13 cc, one boundary of which was the mercury surface in one limb of a mercury manometer. Pressures were read with a cathetometer and temperatures were measured with a calibrated thermometer graduated in 0.02°C intervals. In computing the number of moles of gas formed, a small correction was made for the non-ideal character of the gas. No inert gas was found to be present in the material produced. Two trial runs with ordinary barium carbonate were made. The results of these determinations and of the conversion of the enriched material are given in Table I. It is apparent from the trial runs that quantitative conversions can be made, and it appears that the enriched material is 86.9 percent barium carbonate. The probable presence of impurities had previously been indicated.[1] The enriched carbon dioxide appears quite stable. Some of the material was kept frozen for three months and showed no evidence of decomposition. The enriched gas did not appear to produce material non-condensable in liquid nitrogen. This behavior is perhaps to be expected in view of the comparatively low radiation level (about 4 mc) and the known stability of carbon dioxide under irradiation.[3]

Prior to the analysis of the enriched material a series of tests was made with a 60° Nier-type mass spectrometer on the C^{12}/C^{13} ratio using tank carbon dioxide

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[1] L. D. Norris and A. H. Snell, Phys. Rev. **73**, 254 (1948); Phys. Rev. **74**, 1240 (1949).

[2] Anderson, Libby, Weinhouse, Reid, and Grosse, Phys. Rev. **72**, 931 (1947).

[3] S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons* (The Chemical Catalog Company, Inc., New York, 1928), pp. 109, 155.

of coal origin. The value obtained for the ratio was in good agreement with the data of Nier and Gulbransen.[4] It was found that the conditions for optimum beam were the same for the 44 and 45 peaks, and that, with electrode voltages set for optimum beam, the 44/45 ratio did not change by more than 0.6 percent for an accelerating voltage change of 40 percent. Varying the magnetic field by 20 percent did not change the ratio by more than 0.5 percent. The theoretical treatment of Coggeshall[5] would predict considerable discrimination in the case of electrostatic scanning, but this treatment does not apply without modification to a Nier-type ion source, the focus and beam center electrodes of which should decrease the effect. Inghram[6] has found that large discrimination may occur with electrostatic scanning in this type of instrument if the ion source is in poor focus. In the analysis of the enriched material, magnetic scanning was employed, and the permanent magnet at the ion source was removed in order to eliminate possible discrimination effects.[6]

A portion of the gas was analyzed on the mass spectrometer. It was present at about 100 microns pressure in a large 6-liter bulb in the center of which was a leak of the type used in mass spectrometers of the Consolidated Engineering Corporation, and which was purchased from that concern. Three of the original five parallel leakage paths were eliminated. This arrangement made the correction for change of sample composition with time very small. Preliminary tests with ordinary CO_2 showed that this leak gave molecular flow into the mass spectrometer below 250 microns pressure. For a leak providing molecular flow, discrimination should not occur.[7]

Prior to introduction of the sample for analysis, the spectrometer tube was baked out thoroughly; background in the mass region of interest was less than about 1/20,000 of the subsequent mass 44 peak height. Flowing spectroscopic argon, contained in a bulb immersed in liquid nitrogen, into the spectrometer did not alter this situation.

TABLE I. Conversion of $BaCO_3$ to CO_2.

Run	Moles $BaCO_3$ taken	Moles CO_2 found
Trial I	$0.0_3\,1242$	$0.0_3\,1238$
Trial II	$0.0_3\,4178$	$0.0_3\,4178$
C^{14} sample	$0.0_3\,1761$*	$0.0_3\,1530$

* This value is based on the weight of material, 34.9 mg, as supplied by the Oak Ridge National Laboratory, and a molecular weight of 198.2, involving a correction for the C^{14} content.

TABLE II. Isotopic carbon composition in C^{14} sample.

Percent C^{12}	Percent C^{13}	Percent C^{14}
59.93±0.1	0.67±0.01	39.4±0.1

Thirteen separate scans of the mass spectrum from mass 43 to mass 48 were made. No trend was noted in peak height ratios beyond that resulting from the small change in composition occurring with time in the sampling bulb.[7] A correction was made for this effect. Suitable corrections were made for the C^{13} isotope and for the O^{17} and O^{18} isotopes. The composition of the carbon isotopes in the sample is given in Table II. In the uncertainty estimates, allowance is made for a possible absolute error equal to the probable precision error of the measurements.

Since the 44 and 46 peaks are of approximately the same size, any non-ohmic character in the $4\times10^{10}\Omega$ IRC grid resistor of the FP-54 tube in the detector circuit should be insignificant. Inghram[6] has given detailed information on IRC resistors of the type used. The d.c. amplifier was calibrated with voltages from a Type K-2 Leeds & Northrup potentiometer just before the analysis.

It may be noted that some enriched material, presumably of the same composition as the starting material of this investigation, has been found by Jenkins[8] to be about 40 percent C^{14} by photographic photometry of band spectra of the isotopic C_2 molecules. The value previously obtained[1] for the C^{14} content by the counting of $BaCO_3$ from the same lot as that of the present research is raised from 32 percent to 37 percent by recognizing the existence of impurities. If a half-life of 5600 years instead of 5100 years, is used, the C^{14} content is raised to 40 percent.

In the dilution of the enriched material, a known portion of the latter, contained in a small volume which had been calibrated with mercury, was mixed with a known amount of pure ordinary carbon dioxide contained in a larger volume, also calibrated with mercury. The once-diluted material was again diluted in order to obtain a gas of suitable activity. The smaller volume consisted of the 8-mm bore of a stopcock, together with the sealed-off portion on one side of the stopcock. A ground joint was provided on the other side so that the smaller calibrated volume could be connected to the larger volume. The value of the smaller calibrated volume was 1.8994±0.0003 cm^3 (25°C). An experimentally determined correction of about 0.06 percent was applied to this value for the alteration of volume due to the Apiezon N stopcock lubricant. The larger volume was of about $\frac{1}{2}$-liter capacity and was provided with a small leg for freezing-out purposes. The volumes were chosen so that no pressures measured in the dilution were below about 20 cm Hg. The manometer was constructed from selected 1-in. Trubore tubing. The cathetometer was graduated to 0.005 cm, but the mesicus positions were estimated to 0.001 cm. Temperatures were read with a thermometer graduated in

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[4] A. O. Nier and E. A. Gulbransen, J. Am. Chem. Soc. **61**, 697 (1939).

[5] N. D. Coggeshall, J. Chem. Phys. **12**, 19 (1944).

[6] M. G. Inghram, Phys. Rev. **70**, 653 (1946).

[7] R. E. Honig, J. App. Phys. **16**, 646 (1945).

[8] F. A. Jenkins, Phys. Rev. **74**, 355 (1948).

0.02°C intervals and calibrated by the manufacturer against a standard resistance thermometer. The thermometers were taped to the calibrated volumes. These were surrounded by insulating material, and the whole covered with aluminum foil. In computing the amounts of gas used, a correction was made for gas imperfection.

Following exposure of the glass vacuum system to radioactive material in the dilution procedure, stopcocks were degreased and cleaned, and tank CO_2 was flowed through the system. Following evacuation of the line pure CO_2 was admitted and allowed to stand for several hours. A portion of this gas was then counted to test the efficiency of the decontamination. It was found that activity was not detectable after slowly flowing CO_2 through the system for a 24-hour period. Similar precautions were taken with the calibrated volumes.

The equilibration of the active and inert portions of gas in the dilution procedure was assisted by alternately freezing out and subliming the material, following which a period of about 18 hours was allowed for equilibrium to be established. Whenever material containing C^{14} was frozen before a critical step, several hours were allowed to elapse after sublimation in order to avoid any effects owing to small differences in vapor pressure. Similar precautions were observed in the mass spectrometric analysis.

The pure CO_2 gas used was prepared in a glass vacuum system from anhydrous sodium carbonate and outgassed concentrated sulphuric acid. The CO_2 was dried by several distillations from dry ice temperature and finally by slow passage several times over a 3-foot P_2O_5 tube. The CO_2 was freed from inert gas by cycles of freezing, pumping, and sublimation.

THE COUNTERS

A diagram of the counters used is given in Fig. 1. Close tolerances were held in the machining of the parts. The insulators, 2, were selected pieces of $\frac{1}{8}$-in. Trubore tubing into which the $\frac{1}{8}$-in. Kovar shields, 4, slipped. The holes in the end plugs, 3, were made so as to provide snug fits for the insulators. The relative positions of 2, 3, and 4 in assembly were attained by the use of jigs, and the seals between these parts were made with thinned Glyptal. Baking provided a strong enough seal so that parts did not move appreciably with respect to each other. Small corrections were made for such dimensional changes as did occur. From the dimensions and measurements on the volume of the pumping lead the volume available to gas was known. A central portion of the counter wall was turned down to about 0.010 in. so that counter behavior could be checked with strips of uranium foil. Resolving times were measured by the counting of two approximately equal foils, separately and together, at about the same counting rates encountered in the subsequent work.

Shown in Fig. 1 is a micarta cold reservoir, 8, which was made in two parts which could be clamped together around the counter. Liquid nitrogen in the reservoir provided a satisfactory means of transferring carbon dioxide into the counter quantitatively.

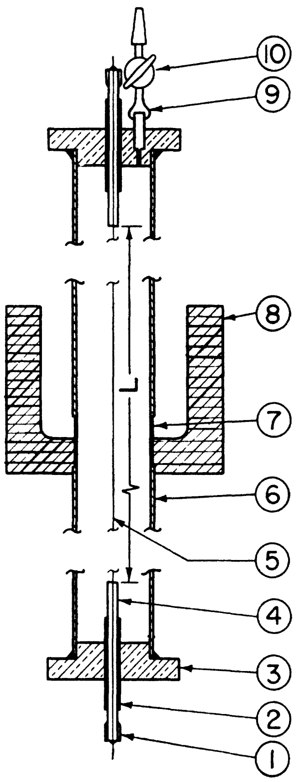

FIG. 1. Cross section of counter. 1—Brass cap. 2—$\frac{1}{8}$-in. Trubore Pyrex tubing insulator. 3—Brass end plug. 4—$\frac{1}{8}$-in. O.D. Kovar shield. 5—0.005-in. Kovar wire. 6—Brass shell, 1 in. O.D., 0.035-in. wall thickness. 7—Wall thickness 0.010 in. in this region. 8—Micarta refrigeration well. 9—Kovar to glass seal. 10—Stopcock and 10/30 standard taper ground glass joint.

The carbon dioxide was present in the counters at partial pressures in the approximate range 1–3 mm Hg. The pressure of the 94 percent argon–6 percent C_2H_5OH quencher gas was approximately 10 or more cm Hg as described later. Under these conditions a satisfactory plateau region is obtainable.

In making an absolute counting measurement on a gaseous radioactive material which is uniformly distributed throughout a counter, it is necessary to know the fraction of the disintegrations which produce counts. This fraction times the total volume available to the gas may be called the effective volume. The size of the effective volume depends on such factors as the distortion of the electric field in the region where the central wire emerges from its shield, the geometry of the end portion of the counter, the pressure, and the particle range. In correcting for the end effect, Libby and co-workers[2] have made use of counters which differ only in length. A similar technique has recently been described by a Canadian group.[9,10] In first approximation the effective volume may be regarded as bounded by the cylinder walls and by planes per-

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[9] Hawkings, Hunter, Mann, and Stevens, Phys. Rev. **74**, 696 (1948).

[10] W. B. Mann and G. B. Parkinson, Rev. Sci. Inst. **20**, 41 (1949).

pendicular to the counter axis at the points where the wire emerges from its shields.

The bare wire length, L, should be replaced, however, by $L-\epsilon$, where ϵ will depend on the factors noted above. Suppose that one has counters of different unshielded wire lengths L (see Fig. 1), which have the same effective cross sections A, and which are filled so as to have the same atomic density of radioactive material ρ. Then the counting rate, R_L, owing to the material of decay constant λ is given by

$$R_L = A\rho\lambda(L-\epsilon), \tag{1}$$

and ϵ can be determined by fitting the data to the linear relationship (1).

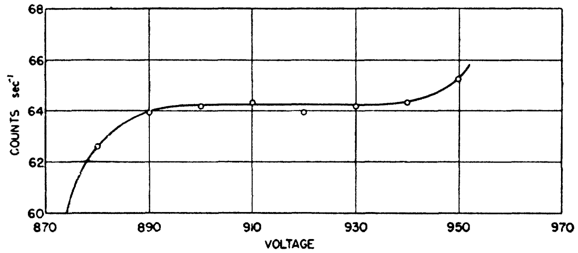

FIG. 2. Counting rate *versus* voltage characteristic for Geiger tube at CO_2 partial pressure of about 2 mm Hg and total pressure 10.0 cm Hg.

In one experiment, three counters, identical except for length, were filled simultaneously to a pressure of 10.0 cm Hg with a carbon dioxide-quencher gas mixture. The partial pressure of the carbon dioxide, which contained enough C^{14} to give convenient counting rates, was about 1.1 mm Hg. Small corrections for resolving time losses, previously determined for gas of this composition, were made. Background corrections were made by utilizing monitor counters with which the master counters had previously been intercompared within the lead shield used for background reduction. The results of this experiment, together with the value of ϵ found, are given in Table III. Column 4 is computed from the least squares line through the data, assuming only counting rates to be uncertain.

Like measurements were made at total pressures of 16.6 and 20.3 cm Hg with counters 1 and 2. The values of ϵ are 0.47 and 0.50 cm at these pressures, respectively. In subsequent counting experiments, only counter 3 was used. The effective volume for this counter is about 90 percent of the total volume available to gas.

It will be shown in the next section that the effective cross section A in Eq. (1) is equal to the geometric cross section of the counter within experimental error.

COUNTING MEASUREMENTS

A known portion of the diluted radioactive carbon dioxide gas was measured in the small calibrated volume referred to previously by making pressure, volume, and temperature measurements. A small correction was made for the non-ideal character of carbon dioxide gas. The pressures measured were in the neighborhood of 10 cm Hg. This material was then quantitatively transferred to the counter by condensing with liquid nitrogen. When the counter had reached room temperature, quencher gas was admitted to the counter to the desired total pressure. Since the quencher enters the counter through a section of capillary tubing, a negligible amount of carbon dioxide should be lost from the counter by back diffusion. This point was checked experimentally by counting the contents of the vacuum line after such a filling. In order to be sure that a uniform concentration of materials existed, the counter was allowed to stand overnight before counting was commenced. Previous experiments had shown that this was sufficient time to allow, since counting measurements over a subsequent 72-hour period showed no change. The background was measured with a monitor counter as above.

Counting data were then obtained as a function of overvoltage. Although the usable voltage range was not long, the counter showed a voltage range where the counting rate was satisfactorily independent of voltage. A plot of counting rate *versus* overvoltage is shown in Fig. 2 for a counter containing CO_2 at about 2 mm Hg partial pressure, the total pressure being 10.0 cm Hg. The material was then counted at the selected position on the plateau for a long enough time to give probable counting errors of about 0.2 percent or better. In most cases duplicate runs were made at a slightly different voltage. The results of the experiments are given in Table IV.

As mentioned, a set of preliminary measurements showed that the counting rate did not change beyond the experimental error over a 72-hour period. The absence of a trend in the counting rate makes it seem likely that no loss of active material was occurring by slow adsorbtion.

TABLE III. Effective length of counters at 10.0 cm Hg pressure.

Counter	L, cm	R_L observed counts/sec.$^{-1}$	R_L calculated counts/sec.$^{-1}$
1	8.674	14.56	14.56
2	21.466	37.13	37.13
3	34.287	59.76	59.76

$\epsilon = 0.42_8$ cm.

TABLE IV. Counting measurements.

Experiment	Half-life, years	Comments
1	5539	CO_2 1.1 mm Hg, total pressure 10.0 cm Hg
2	5586	CO_2 2.3 mm Hg, total pressure 10.0 cm Hg
3	5613	CO_2 3.4 mm Hg, total pressure 10.0 cm Hg
4	5595	CO_2 2.3 mm Hg, total pressure 16.6 cm Hg
5	5613	CO_2 2.3 mm Hg, total pressure 20.3 cm Hg

Average 5589±41 years. The error quoted is the probable error from the above data.

In Experiment 1, no additional carbon dioxide was added to the counter beyond the diluted material containing the C^{14}. In Experiments 2 and 3, additional pure carbon dioxide was added. If active carbon dioxide were being adsorbed on the counter walls, the addition of carrier CO_2 might increase the counting rate. It must be admitted, however, that if the adsorbtion were small, the amounts of inert and radioactive carbon dioxide might be separately proportional to their pressures in the gas; the role of the appreciable amount of quencher gas is not easy to evaluate in this connection. In any case, no indication of a trend in counting rate was observed. In addition, Experiments 4 and 5, in which the total pressure is increased, do not give indication of adsorbtion. While the processes of mixed adsorbtion are complicated it does not seem likely that an appreciable loss in counting rate is occurring because of adsorbtion. Backgrounds of counters which were exposed to activity for considerably longer times than those of the experiments in Table IV did not show any increase in background on pumping out and refilling with quencher. Permanent increases of a few percent in background did occur over very long periods. This behavior may be owing to the deposition of non-volatile radioactive material on counter walls. Preliminary calculations based on the known adsorbtion of carbon dioxide on zinc and copper oxides, and reasonable estimates of the amounts of such materials within the brass counter, had suggested that such absorbtion should be negligibly small.

Experiments 4 and 5, in which the quencher gas pressure was increased, were performed chiefly for the purpose of uncovering a wall effect. The number of β-particles, produced near the counter wall and, failing to produce a count because of too long a mean free path for ion pair formation, should decrease as the pressure is increased. Experiments 4 and 5 do not show such a trend. It seems likely that this observation is connected in part with the very efficient geometry which exists for the detection of backscattered particles. On the basis of these experiments, it is assumed that the effective and geometric counter cross sections are the same.

In the above experiments, account was taken of the slight decrease in effective length of the counters as the pressure increased. Small corrections were made, on the basis of a preliminary experiment, for the effect of CO_2 on the resolving time. Correction was also made for increase in resolving time with total pressure.[11] The total resolving time losses were about 1.3 percent of the observed counting rates.

TABLE V. Comparison of half-life values.

Observers	Half-life, years
Reid, Dunning, Weinhouse, and Grosse[a]	4700±5–10%
Norris and Inghram[b]	5100±200
Hawkings, Hunter, Mann, and Stevens[c]	6100±200
Yaffe and Grunlund[d]	7200±500
This research	5589±75

[a] Reid, Dunning, Weinhouse, and Grosse, Phys. Rev. **70**, 431 (1946).
[b] L. D. Norris and M. G. Inghram, Phys. Rev. **73**, 350 (1948).
[c] See reference 9.
[d] L. Yaffe and M. G. Inghram, Phys. Rev. **73**, 350 (1948).

DISCUSSION OF ERRORS AND COMPARISON WITH OTHER WORK

The probable error derived from the measurements of Table IV is 41 years. Other uncertainties exist, however. An uncertainty of 0.3 percent arises from the mass spectrometric analysis, the dilution factor may be in error by 0.05 percent, and an error of 0.05 percent may exist in the amount of material condensed into the counter. At the higher pressures, the effective counter lengths may be in error by 0.1 percent. Uncertainties of 0.1 percent may exist because of uncertainties in background and resolving time corrections. These known uncertainties raise the probable error in the half-life to 46 years. It seems safer to increase this estimate, however, and the half-life will be taken as 5589±75 years. In Table V the present value is compared with other values which have been obtained for the half-life. Detailed reports have not been given in all cases. Earlier and more uncertain estimates are omitted.*

I thank Arthur Murray for assistance in the preparation of the pure carbon dioxide used in the dilution measurements. I am indebted to the Oak Ridge National Laboratory for the C^{14} material.

This document is based on work performed at the Los Alamos Scientific Laboratory of the University of California under government contract W-7405-eng-36.

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[11] L. Costrell, J. Research Nat. Bur. Stand. **42**, 241 (1949).

* After the present work was submitted for publication the results of a careful measurement of the C^{14} half-life were reported by Engelkemeier, Hamill, Inghram, and Libby, Phys. Rev. **75**, 1825 (1949). This group obtained a value of 5720 years. The uncertainty expressed as the standard deviation was stated to be 48 years, and the "safe" uncertainty was estimated as 100 years.