internuclear distance between fluorine atoms on opposite sides of the molecule was made using the tetrahedral angle for carbon valence bonds and the values of the carbon–carbon and carbon–fluorine distances of 1.50[8] and 1.35 Å., respectively.[9] This calculated distance is 5.38 Å. for the boat form of the molecule. The difference between this and the observed "diameter" leaves the fluorine atom a van der Waals radius of only 0.85 Å, a value to be compared with 1.35 Å given by Pauling.[10] Other instances in which a lack of space for rotation of molecules has been noted have been explained as due to interpenetration[5] or oscillation rather than complete rotation.[6] It may very well be that the van der Waals radius of a fluorine atom in a fluorocarbon molecule is less than 1.35 Å. This would be in accord with the known variability of the van der Waals radius and the abnormally small values for carbon–carbon and carbon–fluorine bond distances in molecules in which two or more fluorine atoms are bonded to a single atom of carbon.[8,9]

Summary

The compound C_6F_{12} (probably dodecafluorocyclohexane) forms face-centered cubic crystals with a = 10.00 kx. in which the molecule has an apparent diameter of 7.07 kx. Properties of the solid form of the substance indicate that its molecules probably rotate down to a temperature of about −105°. At this point a transition occurs which may be due to the cessation of the rotation. The crystals sublime at 51° under 760 mm. pressure and melt when confined at about 58.2°. The solid has a density of 1.93 g. per ml. at 23°.

SEATTLE, WASHINGTON RECEIVED MAY 12, 1947

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[8] Karle and Brockway, THIS JOURNAL, **66**, 574–584 (1944). These authors give the value for the carbon–carbon distance in the dimer of trifluoracetic acid as 1.47 ± 0.03 Å.

[9] Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

[10] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 176.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEENS COLLEGE]

The Quantitative Measurement of Tritium: Hydrogen–Alcohol–Argon Mixtures

BY MAXWELL LEIGH EIDINOFF

Introduction

The development of methods for the quantitative determination of tritium is of value inasmuch as its thirty-one year half life[1] and availability render its use as a tracer element very advantageous. Tritium activity has been measured by introducing into a Geiger–Müller counter tube active butane,[2] active water vapor plus propane,[3] active hydrogen plus ethanol vapor.[4,5] Black and Taylor,[6] in a careful study of the hydrogen–water isotope equilibrium, used a counting gas mixture containing hydrogen, water vapor, argon and ethanol. The plateau characteristics and convenience of measurement are influenced by the composition and partial pressures of the counting mixture constituents and the dimensions of the counter. Recently a procedure for tritium determination using a quartz ionization chamber attached to a Lauritsen electroscope has been described by Henriques and Margnetti.[7] Since the argon plus ethyl alcohol counting mixture has been used extensively in counter research, it was decided to study the hydrogen–argon–ethyl alcohol system as a quantitative procedure for the measurement of tritium.[8] This paper describes apparatus and procedures developed and results obtained.

Experimental

Geiger-Müller-Counter Tubes.—Several counter tubes having the dimensions shown in Fig. 1 were used in this investigation. The glass envelope and tunsten-glass seals permit ready degassing and vacuum tightness over extended periods of use. A useful improvement in design has been provision for a capillary tube and stopcock and a large bore stopcock. The former minimizes diffusion of gases from the tube during the filling operation while the latter, leading directly to the high vacuum line, permits more rapid evacuation of the tube between successive fillings. The effective counting volume is about 200 cc. Although ceiling illumination did not significantly affect the measured counting rates, the counters were shielded from light by a dark cloth during the measurements. One tube was permanently surrounded by a $^3/_8$ inch lead shield to reduce laboratory background variations.

Filling Line and Bank of Counters.—The gas mixing lines are illustrated in Fig. 2 with the exception of the high vacuum system. The manometer and McLeod gage (H) permit convenient control over the quantity of gas admitted up to the beginning of the capillary tubing manifold (K). The latter minimizes gas dead space above the counter tubes and back diffusion of the gases in the counter tube during the filling operation. As a result of a pressure differential, gas flows into the counter tubes through the capillary (M). A Zimmerli gage[9] (not shown in Fig. 2) was found accurate to 0.1 mm. pressure and was used in many fillings in place of the vacuum end manometer (L).

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[1] R. D. O'Neal and M. Goldhaber, *Phys. Rev.*, **58**, 574 (1940).

[2] T. M. Powell and E. B. Reid, THIS JOURNAL, **67**, 1020 (1945).

[3] B. J. Fontana, *ibid.*, **64**, 2503 (1942).

[4] M. B. Allen and S. Ruben, *ibid.*, **64**, 948 (1942).

[5] W. F. Libby and C. A. Barter, *J. Chem. Phys.*, **10**, 184 (1942).

[6] J. F. Black and H. S. Taylor, *ibid.*, **11**, 395 (1943).

[7] F. C. Henriques, Jr., and C. Margnetti, *J. Ind. Eng. Chem., Anal. Ed.*, **18**, 420 (1946).

[8] A hydrogen–helium–ethyl alcohol counting mixture is briefly described by A. F. Reid in the monograph "Preparation and Measurement of Isotopic Tracers," J. W. Edwards Co., Ann Arbor, Mich. (1946).

[9] Made by Scientific Glass Apparatus Co., Bloomfield, N. J.

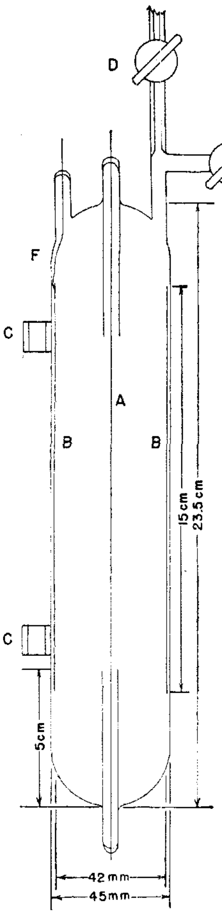

Fig. 1.—Geiger counter tube used for tritium counting: A, tungsten wire anode (4 mil.); B, copper gauze cathode, 100 mesh, 15 cm. × 42 mm. diameter (no prior conditioning); C, glass supports for sealed ampules containing uranium salt solutions; D, capillary stopcock to filling line; E, stopcock to high vacuum line; F, glass envelope, 45-mm. Pyrex tubing.

Materials.—The most active tritium sample,[10] stored in (B) Fig. 2, was diluted using gas bulbs A, G and F with purified inactive hydrogen. The HT, diluted sufficiently so as to furnish an activity of about 100 counts per minute per mm. pressure at 25° in the counter shown in Fig. 1, was stored in bulb (F), Fig. 2. Argon (Ohio Chemical Co.) was passed slowly through a magnesium-packed tube at 625°, a copper oxide packed tube at 350°, tubes containing soda lime and phosphorus pentoxide and the purified gas was stored in (C), Fig. 2. Tank hydrogen was passed through tubes containing calcium chloride, soda lime, platinized asbestos at 300° and phosphorus pentoxide. Ethyl alcohol (absolute, Commercial Solvents Co.) was vacuum distilled into the alcohol reservoir of the filling line (E) after refluxing over calcium oxide. Inasmuch as the effect of gas impurities on Geiger–Müller counter tube functioning has not yet been adequately explored, it was decided to purify the gases and vapors used in the manner described above.

Electronic Equipment.—A Neher-Pickering quenching circuit and pre-amplifier[11] was used to insure good extinguishing action in the counter gas mixtures. The grid and cathode resistors had resistances of 10 and 1.5 megohms, respectively. The counting mixture has self-quenching properties. It was observed that the use of the Neher–Pickering unit furnished a broader plateau as compared with experiments where the latter was not used. Counting measurements were made using a scale of 64 circuit and an electronically stabilized d.c. voltage supply continuously variable to 2000 volts. Counting pulse shapes and number were examined at intervals using a cathode ray oscilloscope. Checks of the functioning of the scaling circuits were made from time to time by counting a standard uranium sample using a thin-walled glass silvered cathode counter tube. These checks showed a deviation of less than 0.5% over the period of the measurements.

Additional Details of Procedure.—Background counting rates were measured using an inactive gas mixture having the same partial pressures of hydrogen, argon and ethanol as the mixtures containing HT. This rate was about 200 counts per minute. The active sample was introduced after a fifteen-minute pumping period. The gases were introduced in the order: hydrogen, ethyl alcohol, argon. Following the counting rate measurement, the tube was pumped out for about two hours at a pressure of less than 10^{-4} mm.

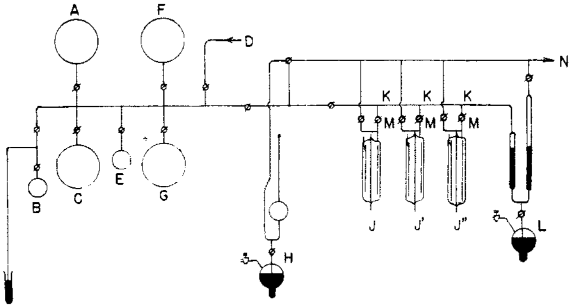

Fig. 2.—Gas lines and bank of counter tubes for tritium counting: A, purified inactive hydrogen, 5 liter; B, active tritium sample, 100 ml.; C, argon, 5 liter; D, line from experimental tritium sample; E, ethyl alcohol, 50 ml.; F, diluted tritium-containing gas, 5 liter; G, auxiliary HT reservoir and gas source for preparation of HTO; H, combination closed end manometer and McLeod gage for 1–20 mm. range. J,J′,J″, bank of glass envelope copper gauze cathode Geiger counter tubes; K, capillary tubing manifold; L, vacuum end precision manometer; M, capillary stopcocks; N, to McLeod gage and high vacuum system.

The observed counts were corrected for the resolving time correction using the experimentally determined $T_d = 2.5 \times 10^{-4}$ second. At about 3000 counts per minute, the highest counting rate used in this investigation, the correction is slightly more than one per cent. At 1000 counts per minute, the correction is less than 0.5%.

During the early experiments, the constancy of the counting efficiency of a tube was checked by inserting a sealed ampoule containing a uranium salt solution in a well defined position outside the counter tube using the supports (C), Fig. 1.

Results

Counting Rate–Voltage Characteristics.—A threshold voltage of approx. 1250 volts (measured directly across the counter tube electrodes) was observed for the gas mixture containing 25, 20–25, 20–25, mm., respectively, of hydrogen, ethanol and argon. For this gas composition, counter tubes having the dimensions given in Fig. 1 have a plateau of 20–40 volts beginning about 50 volts above the threshold voltage. In measuring the activity of a sample, counting rates were measured at 10- or 20-volt intervals for a 120-volt range and the plateau ordinate was obtained from a plot of these points. In this plateau region, the pulses as observed on an oscilloscope screen are well defined and of almost uniform height. The counting rate starts to rise steeply at about 140 volts above the threshold voltage. Numerous plural pulses are observed on the oscilloscope screen in this voltage region. Approximately 15,000 counts were obtained at each voltage setting for the samples cited in Tables I and II. Approximately 2000 counts

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(10) Obtained as HT from the Physics Department of Columbia University.

(11) The pre-amplifier (Model EX-7) and scaling unit (GS-4) were made by Technical Associates, Glendale, Cal.

were obtained at each voltage setting in measuring the background.

Counting Rate *vs.* Partial Pressure of Active Sample.—The partial pressure of the HT was varied over the range 10 to 25 mm. in a number of experiments. The gas composition was maintained close to 25, 20–25 and 20–25 mm. of hydrogen, argon and ethyl alcohol, respectively. Constancy of the counts per minute per mm. HT was observed within one to two per cent., approximately the precision of the measurements. The results of one such set of measurements are given in Table I and plotted in Fig. 3. It may be noted that the total pressure ranged from 65 to 75 mm. with smaller variations in the ethyl alcohol and argon pressures.

TABLE I

COUNTING RATE *vs.* HT PARTIAL PRESSURE, COUNTER TUBE NO. 1

Pressure, mm. at 25°					Counts[a] per minute × 10⁻³	Counts[a] per per mm. minute HT
HT	Total H_2	Ethyl alcohol	Argon	Total		
10.8	25.5	20	19.5	65	1.14	106
17.0	24.5	21	22	67.5	1.82	107
25.0	25.0	25	25	75	2.66	106

[a] Corrected for background counting rate (approx. 0.20 × 10^3 counts per minute).

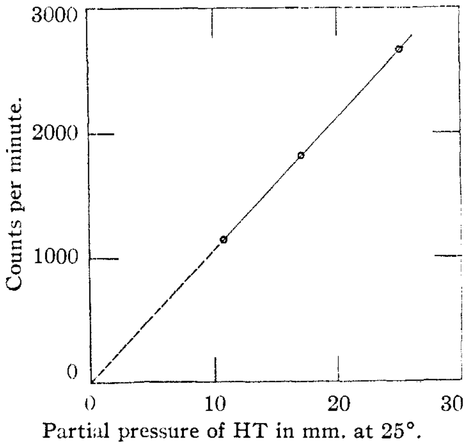

Fig. 3.—Counting rate *vs.* partial pressure of tritium sample. Composition of gas counting mixture: hydrogen, ethyl alcohol and argon at partial pressures of 25, 20–25 and 20–25 mm., respectively, at 25°.

Reproducibility of Tritium Counting Rates.—In order to check the reproducibility, four or five consecutive counter tube fillings were made using the same HT sample. Background counts were made at frequent intervals using inactive gas mixtures. The results for two counters of approximately the same dimensions are given in Table II. Two samples of slightly different activity were used with counter No. 1.

The average deviation of the counts per minute per mm. HT is less than one per cent. The satisfactory agreement demonstrates that the procedures described above represent a convenient quantitative method for the estimation of tritium in the form of hydrogen gas.

TABLE II

TRITIUM COUNTING DATA

	Pressure, mm. at 25°				Counts[a] per minute × 10^{-3}	Counts[a] per minute per mm. HT
	HT	Ethyl alcohol	Argon	Total		
Counter	23.2	21	24	68	2.66	115
no. 1	21.4	23	25	69	2.47	115
Sample	25.3	25	28	78	2.92	115
no. 1	21.2	24	23	68	2.43	115
Counter	22.6	25	21	69	2.99	132
no. 1	23.3	27	22	72	3.05	131
Sample	23.1	25	28	76	3.07	133
no. 2	23.1	27	25	75	3.07	133
	23.4	22	23	68	2.73	117
Counter	22.1	23	25	70	2.62	118
no. 2	23.7	23	22	69	2.79	118
Sample	25.3	24	21	70	2.99	118
no. 1	23.3	25	22	70	2.77	119

[a] Corrected for background counting rate (approx. 0.20 × 10^3 counts per minute).

Discussion

The energy of the beta particle emitted by tritium is about 15000 e.v.[12] Brown[13] reported that the maximum range in helium at atmospheric pressure is 13 ± 1 mm. The specific ionization per unit pressure of the argon–alcohol mixture is several-fold times that for helium. Since it is only necessary to have one electron formed inside the counter to initiate the Geiger–Müller tube pulse, it follows that practically every beta particle in the sensitive region of the counter tube will be counted. In the absence of significant surface adsorption effects it follows from this consideration that the counts per minute per mm. HT should be independent of the HT partial pressure and minor variations in the over-all chemical composition of the hydrogen–argon–ethyl alcohol mixture used. This is in agreement with the results shown in Table I and II.

The utilization of the procedures described above employing a bank of counter tubes sealed to the same filling line and one or more scaling circuits makes it possible to carry out a satisfactorily large number of tritium determinations in a given interval.

When tritium is employed as a tracer in reaction studies, it is frequently necessary to determine the tritium content of the combustion product HTO. Preliminary experiments have indicated that degassing problems are significant when using the latter compound. Water vapor may in addition give rise to negative ions in the counter discharge

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(12) R. D. O'Neal, *Phys. Rev.*, **60**, 359 (1941).

(13) S. C. Brown, *ibid.*, **59**, 954 (1941).

leading to the possibility of spurious counts.[14,15] Consequently the procedure used in our laboratory has been the quantitative conversion of HTO to HT and the measurement of the activity of the latter.[16,17]

Acknowledgments.—The author wishes to thank Mr. Karl Schumann of Columbia University for constructing the Geiger–Müller counter tubes. Mr. Edward J. Kuchinskas assisted in the counting measurements. A grant-in-aid from the Research Corporation made it possible to carry out this investigation.

Summary

Apparatus and techniques are described for the quantitative measurement of tritium in a hydrogen–argon–ethyl alcohol counting mixture. The counting rate is proportional to the partial pressure of the active hydrogen sample over the range of pressures studied. Average deviations found in tests of counting rate reproducibility are less than one per cent.

FLUSHING, NEW YORK RECEIVED APRIL 30, 1947

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[14] S. Korff, "Electron and Nuclear Counters," D. Van Nostrand Co., New York, N. Y., 1946, p. 82.

[15] C. G. Montgomery and D. D. Montgomery, *Phys. Rev.*, **57**, 1030 (1940).

[16] M. L. Eidinoff, THIS JOURNAL, **69**, 977 (1947).

[17] T. H. Norris, S. Ruben and M. B. Allen, *ibid.*, **64**, 3037 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, QUEENS COLLEGE]

The Cathodic Protium–Tritium Separation Factor. I. Apparatus; Platinum Cathode–Alkaline Solution[1]

BY MAXWELL LEIGH EIDINOFF

Measurement of the electrolytic isotope separation factor for the hydrogen isotopes of atomic weights one and three should yield results relevant to the theory of the familiar process for deuterium enrichment, the exhaustive electrolysis of water. Inasmuch as this theory involves assumptions concerning electrochemical processes at the cathode, the data should make possible a more thorough appraisal of the current status of this theory. Of more restricted interest is the observation that the protium–tritium factor involves the largest percentage difference in isotopic masses and should therefore be the largest unit process separation factor obtainable. This paper describes the electrolysis cell, electrode gas train and procedures developed for the measurement of the protium–tritium cathodic separation factor. Results are reported using a smooth platinum cathode at 20° in an alkaline medium containing approximately 10^{-11} atom fraction tritium and normal deuterium abundance.

The quantity of cathode gas required for a measurement of the separation factor is about 2×10^{-3} mole of hydrogen. The isotopic composition of the electrolytic solution is essentially constant during a run. The separation factor, $\alpha_{\text{H-T}}$ is equal to $(\text{H/T})_{\text{gas}}/(\text{H/T})_{\text{liquid}}$ or, equivalently, $(\text{T/H})_{\text{liquid}}/(\text{T/H})_{\text{gas}}$, where H and T refer to the number of the respective atoms in the phases indicated. Since the tritium atom fraction is so small, the numerator and denominator of the latter expression for α are proportional to the radioactivity of a hydrogen gas sample from each phase, where the activity is defined as counts per minute per millimeter pressure of hydrogen at 25° inside the same Geiger counter tube. The counting gas mixture contained 25, 20–25 and 20–25 mm., respectively, of hydrogen, argon and ethyl alcohol. The tritium activity of the alkaline solution was determined by quantitatively converting the hydrogen in about 0.05-g. solution samples to hydrogen gas over magnesium at 625° in an analytical train previously "seasoned" at this activity.

Experimental

Details of construction of the Geiger counter tube, filling train, purification of hydrogen, argon and ethyl alcohol, and electronic equipment and counting procedures have already been described by the author.[2] The radioactive water was prepared by passing a properly diluted HT sample over copper oxide wire at 350° and condensing the product in a trap cooled by Dry Ice.

Electrolysis Cell and Electrode Gas Lines (Fig. 1).—The design was influenced by the following considerations: (a) contaminating gases must not be present in the cathode lines; (b) diffusion of anode compartment oxygen gas bubbles must be avoided and diffusion of dissolved oxygen reduced to a minimum; (c) a maximum fluctuation of 3 cm. equivalent differential water head pressure could be tolerated; (d) limited samples of radioactive water were at hand; (e) ready interchangeability of various electrode materials was desired and (f) thermostatic control of the electrolysis cell was desired.

The electrode compartments (A) and (A′) are made from 10 mm. i.d. tubing containing about 5 ml. of electrolyte and separated by a 30-ml. length of 2 mm. capillary tubing (F). The electrodes enter the electrode compartments by a weld to tungsten wire that emerges from the Pyrex standard taper joint top in a glass seal. In filling the cell, the electrolyte medium is added from the reservoir (E) into the evacuated cell. The gas volumes (H) and (H′) were selected so that practically equivalent gas pressures are maintained over the solution despite the 2:1 ratio by volume of gases evolved. Occasional addition of oxygen gas *via* bulb (G) suffices to maintain a balanced pressure. Using approximately 10% sodium hydroxide solution as medium and 91 volts across the electrodes, the

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[1] Presented at the April 1947 meeting of the American Chemical Society at Atlantic City, N. J. Preliminary communication published in THIS JOURNAL, **69**, 977 (1947).

[2] M. L. Eidinoff, *ibid.*, **69**, 2504 (1947).