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

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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.

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, α_{H-T} is equal to $(H/T)_{gas}/(H/T)_{liquid}$ or, equivalently, $(T/H)_{liquid}/(T/H)_{gas}$, 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
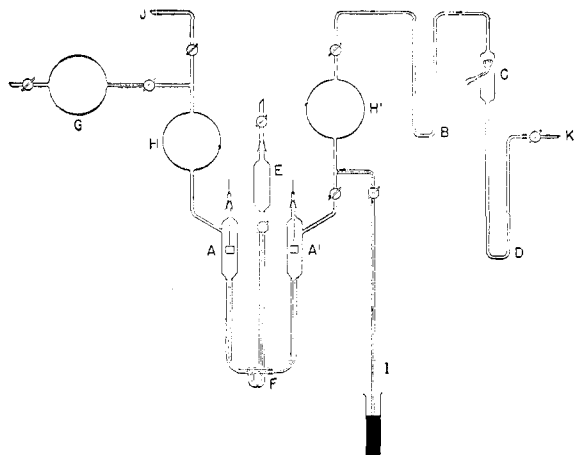
Fig. 1.—Electrolysis cell and electrode gas lines: A, anode compartment; A', cathode compartment; B, liquid air-cooled U tube for water vapor stripping; C, hot wire combustion chamber for eliminating oxygen traces; D, liquid air-cooled U tube for water vapor stripping; E, reservoir and filling tube containing NaOH–NaOT solution; F, 2-mm. capillary tubing; G, 200-ml. bulb containing oxygen; H, oxygen collecting bulb; H', hydrogen collecting bulb; I, pressure indicator during electrolysis; J, to vacuum system; K, to Geiger counter filling system.

electric current is 40 milliamperes, corresponding to a cell solution resistance of about 2200 ohms. In a two-hour electrolytic run, approximately 0.03 g. of water is electrolyzed. Under these conditions the solution bathing the cathode is well stirred owing to the vigorous evolution of gas bubbles. Gas bubbles are not observed in (F). The hydrogen gas collected in (H') is stripped of its water vapor content in liquid-air cooled tube (B), of oxygen traces in the hot wire combustion tube (C) and of the resulting water vapor in (D).

Analysis of Tritium from Solution (Fig. 2).—The design was influenced by the following considerations: (a) the total hydrogen content of approximately 0.03 g. of 10% sodium hydroxide solution must be quantitatively converted to hydrogen gas; (b) the time required for the conversion should be reasonably short; (c) since the hydrogen obtained may be about fifteen times more active than the cathode gas, means should be provided for accurate dilution of the former with ordinary hydrogen in order to increase the accuracy of the separation factor calculation; (d) apparatus used in conversions should be first "seasoned" with the radioactive water and hydrogen in order to avoid serious dilution with light hydrogen adsorbed on the walls.

Approximately 0.03–0.05 g. of the alkaline solution is rapidly added to the reservoir (E) using a specially designed pipet. Prior to this, (E) has been dried, "seasoned" and filled with nitrogen gas that has entered (E) via (A) and the phosphorus pentoxide tube (C). After the solution is solidified using a Dry Ice-trichlorethylene bath, the nitrogen is pumped out and carbon dioxide added at (B). The Dry Ice-bath is replaced by a bath of warm water. The volume (E), about 50 ml., was selected in order that the carbon dioxide added should suffice for the conversion of the sodium hydroxide to sodium bicarbonate. After two hours, U tube (F) is surrounded by a Dry Ice-bath and the lower half of (E) brought to a temperature of 350° in order to convert the sodium bicarbonate into carbon dioxide, water and sodium carbonate. The carbon dioxide is pumped out through (D) and the water is collected in (F).

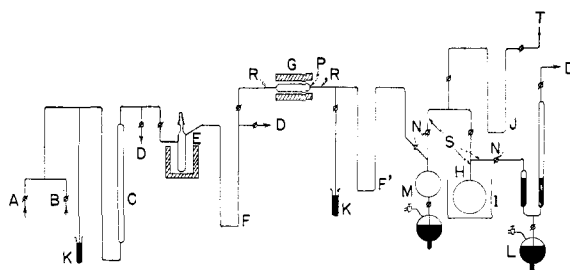In the meantime the quartz tube (P) packed with mag-

Fig. 2.—Train for analysis of tritium content of alkaline solution: A, nitrogen supply; B, carbon dioxide supply; C, phosphorus pentoxide drying tube; D, to vacuum system; E, 50-ml. receiver for NaOH–NaOT sample; F,F', Dry Ice-cooled U-tube for water stripping; G, tube furnace; H, 500-ml. gas collecting bulb; I, water-bath thermostat; J, Dry Ice or liquid air-cooled U tube; K, safety blowoff and pressure indicator; L, constant volume vacuum manometer; M, 150-ml. Toepler pump; N, capillary stopcock; P, quartz tube containing magnesium turnings; R, quartz–Pyrex graded seals; S, capillary tubing; T, to Geiger counter filling system and vacuum lines.

nesium chips and sealed into the line with graded Pyrex-quartz seals (R) has been maintained at 625° and pumped out for several hours. After closing stopcock (N) and removing the cold trap from (F) the water vapor is converted by reaction with the magnesium to hydrogen. The normally slow transfer of the water vapor from (F) into the heated tube region is accelerated by repeated transfer of the hydrogen produced using the Toepler pump (M). The resulting hydrogen is collected in the water-thermostated 500-ml. bulb (H) until the indicator (K) shows no further pressure change. Accurate dilution of the gas in (H) is effected by use of the Toepler pump (M), an outside source of ordinary purified hydrogen and the constant volume mercury filled vacuum end manometer (L), the levels of which are read by a cathetometer precise to 0.05 mm.

Results

The results of two electrolysis experiments at 20.0° using a smooth platinum foil cathode in 10% alkali solution and a current density of 0.1 amp. per sq. cm.[1] are presented in Table I.

TABLE I

PROTIUM–TRITIUM SEPARATION FACTOR

| Hydrogen source	Tritium activity in counts per minute per mm. hydrogen at 25°			Isotope separation factor
Alkali solution	574	568	570 Av. 571	
Cathode gas				
Electrolysis 1	38.9			14.7
Electrolysis 2	42.7			13.4

The tritium activity from the alkaline solution was determined in the manner described above. The hydrogen was converted to hydrogen gas in three independent determinations following a preliminary "seasoning" of the analytical train. Each of these three values is the average for several independent fillings of the counter tube. The average deviation for the latter was less than 1% and the largest spread of results less than 2%. The check among the three results for the alkali solution demonstrates that the analytical method described above is satisfactory.

The second electrolysis was carried out after an interval of several weeks during which time the platinum electrode was immersed in the alkaline solution. The oxygen content of the cathode gas was shown to be negligible. In one filling, the hot wire combustion tube was omitted. No significant difference in sample activity was found. This result was anticipated, since gas bubbles could not be detected in the capillary tube (F) of Fig. 1. The measured background counting rate was about 200 counts per minute for an inactive gas mixture having this composition. The data given in Table I have been corrected for background. The counting technique used has been shown to yield results reproducible to about 1%.[2] The activity per mm. of active sample was found to be constant to about 1%. The tritium samples obtained from the alkali solution were diluted with ordinary hydrogen by a factor of about five in order to bring the resulting activity closer to that for the cathode gas. The error incurred in the gas dilution is less than 0.2%. The isotope separation factors in the last column of Table I are considered reliable to better than 3%.

Discussion

From the discussion of errors given above, it is probable that the variation in the two separation factors is caused by slight differences at the platinum cathode surfaces during the electrolyses. Such variations have been noted in the measurement of the protium–deuterium factor.[3,4,5]

If thermodynamic isotope exchange equilibrium prevailed at the cathode surface, then the isotope separation factor defined above would be approximately equal to the equilibrium constant of the gaseous reaction

$$HT + H_2O \rightleftarrows H_2 + HTO \qquad (1)$$
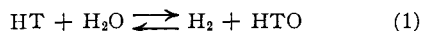
When the H_2O–HTO system is considered ideal, the two quantities differ by the vapor pressure ratio of these isotopic species. The equilibrium constant at 20.2° for reaction (1) has been reported to be 6.47 ± 0.12 by Black and Taylor.[6] Libby calculated a value of 6.24 for this equi-

librium at 20°.[7] The protium–tritium ratio for the hydrogen gas in the electrolyses reported above is thus slightly more than twice as large as that corresponding to thermodyanamic equilibrium prevailing at the electrode surface.

In the case of the protium–deuterium factor, results ranging from 6 to 8 have been obtained at a smooth platinum cathode in both acid and alkaline medium.[3,4,5] The equilibrium constant for the gaseous reaction

$$HD + H_2O \rightleftarrows H_2 + HDO \qquad (2)$$
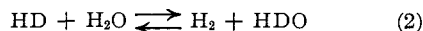
has been calculated from molecular data by Libby.[7] At 20°, the latter value is 3.78. In this case the protium–deuterium ratio in the cathode gas ranges from 1.6 to 2 times that corresponding to thermodynamic equilibrium. At a platinized platinum electrode, the observed separation factor is close to the equilibrium conditions for equation (2). The latter conditions would be expected to prevail, since isotopic exchange is rapid at a platinized surface.

Using the apparatus described above and an electrolyte medium containing the atom fraction tritium stated above together with several atom per cent. deuterium, it will be possible to obtain simultaneous protium–deuterium and protium–tritium separation factors. The ratio of these factors, measured under identical electrode conditions, should furnish valuable data for the application of the theory proposed by Okamoto[8] and by Eyring, Glasstone and Laidler.[9]

Summary

Apparatus and techniques are described for the the measurement of the cathodic protium–tritium isotope separation factor from alkaline solutions.

Separation factors of 13.4 and 14.7 were obtained in the electrolysis at 20.0° of a 10% sodium hydroxide solution at a smooth platinum foil cathode using a current density of 0.1 amp./sq. cm.

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