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TRITIUM SEPARATION FACTOR IN THE CALCIUM-WATER REACTION

by

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ABSTRACT

The separation factor for hydrogen and tritium was found to be 1.8 in the reaction of tritiated water and calcium metal at 85 to 95°C. An ionization chamber was calibrated with standards of tritiated water and the calibration data were combined with this separation factor to yield a calibration curve for tritiated hydrogen gas samples.

CONTENTS

TRITIUM SEPARATION FACTOR IN THE CALCIUM-WATER REACTION

INTRODUCTION

Johnston and Davis(1) reported a separation factor ($\alpha_{H/D}$) of 1.41 in the reaction of D_2O-H_2O mixtures with calcium at 27°C. Reference to the separation factor in the reaction of T_2O-H_2O mixtures with calcium was not found in the literature.

The method(2) generally used for determining small concentrations of tritium in water involves reaction of the tritiated water with calcium metal, followed by ion chamber measurement of the current carried by a portion of the liberated gases. Primarily because the rates of reaction of calcium with the isotopic forms of water are different, the gas which is actually analyzed differs in tritium content from the liquid sample of interest. Normally, as a calibration technique, standards of tritiated water are converted to hydrogen by the same reaction and the effect of isotopic separation is thus eliminated. However, a knowledge of the separation factor ($\alpha_{H/T}$) in this reaction is required when the tritium content of a gas is to be determined, since the method is calibrated by the analysis of tritiated water standards rather than gaseous standards.

SUMMARY

The separation factor for hydrogen and tritium was found to be 1.8 in the reaction between tritiated water and calcium metal at 85 to 95°C, at low concentrations of tritium.

The experimental method involved comparing the ion chamber currents from two tritiated hydrogen samples, one produced by the complete decomposition of tritiated water over zinc at 400°C and the other produced by the reaction of another sample of the same tritiated water with calcium at 85 to 95°C.

The separation factor was not a sensitive function of the extent of the calcium-water reaction, and thus may be applied to routine analyses where the reaction is not closely controlled.

DISCUSSION

APPARATUS

The apparatus used for the decomposition of tritiated water by reaction with zinc was the same as that given by Kirschenbaum(3).

The apparatus used for analysis of tritiated water by reaction with calcium and for ion chamber measurements on the liberated hydrogen was essentially the same as that described by Wilzbach et al.(2) The water sample was reacted with calcium metal in a glass reaction flask and the evolved gas was admitted to the ion chamber through a drying tube.

EXPERIMENTAL METHOD

Aliquots of a sample of tritiated water were reacted with hot zinc metal and calcium metal. Since the zinc reaction completely decomposed the water, the tritium content of the hydrogen product was the same as that of the water. The ratio of the tritium content of the hydrogen product of the incomplete calcium reaction to that of the zinc reaction was determined by measuring the ion chamber currents from the two hydrogen samples. The separation factor ($\alpha_{H/T}$) for the calcium reaction was computed as shown in the section on calculations.

The reactions are as follows:

$$Zn + H_2O \xrightarrow{400^\circ C} ZnO + H_2$$

$$Ca + 2H_2O \xrightarrow{85 - 95^\circ C} Ca(OH)_2 + H_2$$

For the zinc-water reaction, three runs were made with water that contained 0.83 millicurie of tritium per milliliter. This solution was prepared by dilution of a known standard solution. In each run, 0.7 milliliter of the tritiated water was used. Complete decomposition of the water was indicated by (a) its vaporization and disappearance from the sample tube, (b) the absence of water in the cold trap on the downstream side of the furnace, and (c) the buildup of hydrogen pressure in the storage bulb to approximately the calculated value.

After each run, the gas in the storage bulb was analyzed on the mass spectrometer. The gas was then expanded into the evacuated ionization chamber where the pressure and ion current were read.

For the calcium-water reaction, the same tritiated water was analyzed in duplicate. This average value was then used in the calculations for the three runs with zinc as shown in the table on page 6. The procedure involved the following steps: (a) adding three grams of coarsely ground calcium to the reaction flask, (b) evacuating the system to 0.1 mm or less, (c) slowly adding 3 ml of the tritiated water sample to the calcium, (d) drying and expanding the liberated gas into the ionization chamber, and (e) reading the pressure of the gas and measuring the ion current.

RESULTS

The experimental results are summarized in the table on page 6. The ion current measurements from the experiments with the zinc-water reactions are corrected for pressure and for the increased ionization due to the presence of oxygen and nitrogen in Runs 1 and 2. The average ion currents for the gas from the calcium-water reactions are corrected for pressure also, so that the ion currents are on a comparable basis.

In routine analyses with the calcium-water reaction, it was found that approximately one-half of the theoretical volume of gas was obtained, i.e., the reaction between water and calcium went only about halfway to completion. Therefore, in the calculation of the separation factor, the reaction was taken to be 50 per cent complete. As shown in the following section, small variations in the extent of reaction have only a minor effect on the experimentally determined value for alpha.

The reported separation factor is the average of results from the three runs. Air was admitted to the system during the run through small cracks that were formed in the reaction tube. Corrections were based on ionization efficiency curves similar to those given by Wilzbach et al.(2) Pressure corrections were made from measurements of ion current versus pressure at constant tritium content.

SUMMARY OF EXPERIMENTAL RESULTS

Run No.	Gas Composition	Corrected Ion Currents amperes x 10^{11}	I/I_o (equiv. T/T_o)	$\alpha_{H/T}$
Calcium-water (duplicate)	-	6.80 6.80	-	-
Zinc-water				
1	96.4% H_2 2.95% N_2 0.63% O_2	12.7	0.536	1.98
2	84.4% H_2 15.1% N_2 0.34% O_2 0.17% A	11.2	0.608	1.74
3	99.8% H_2 0.17% N_2 0.01% O_2	11.0	0.619	1.71
			Average	1.81

CALCULATIONS

The separation factor, $\alpha_{H/T}$, for hydrogen and tritium from the calcium-water reaction may be expressed by the general equation,

$$\alpha_{H/T} = \frac{\ln \; 1 - \frac{HW}{H_oW_o}\Big]}{\ln \left[1 - \frac{TW}{T_oW_o}\right]} \qquad (1)$$

where the symbols have the following significance:

H_o = mol fraction of hydrogen in the charge

H = mol fraction of hydrogen in the composite gas product

T_o = mol fraction of tritium in the charge

T = mol fraction of tritium in the composite gas product

W_o = mols of charge

W = mols of product gas

For the calcium-water reaction:

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

$$W = \frac{ZW_o}{2} \qquad (2)$$

where Z is the fraction of completion of the reaction (Z may vary from 0 to 1). Substituting this value of W in Equation (1), one obtains

$$\alpha_{H/T} = \frac{\ln\left[1 - \frac{HZ}{2H_o}\right]}{\ln\left[1 - \frac{TZ}{2T_o}\right]} \qquad (3)$$

Since the quantity of tritium on a molar basis is extremely small compared to the quantity of hydrogen in the water sample, $H = H_o = 1$. The ratio T/T_o was taken as the same as the ratio of the corrected ion currents from the zinc-water and calcium-water reactions, as shown in the table on page 6. The ion current is directly proportional to the tritium content of the gases, for all practical purposes.

Substituting the appropriate values from Run 3, for example, for the quantities in Equation (3), one obtains

$$\alpha_{H/T} = 1.71$$

The quantity T/T_o will vary with Z. To determine the dependence of T/T_o on Z, Equation (1) was transformed to give

$$\frac{T}{T_o} = \frac{2}{Z}\left[1 - \left(1 - \frac{Z}{2}\right)^{1/\alpha}\right] \qquad (4)$$

In this equation, if $\alpha_{H/T}$ is held constant at 1.71 and Z is allowed to vary from 0 to 1, the variation of T/T_o is shown in the following table:

THE VALUE OF T/T_o AS A FUNCTION OF Z

Z	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T/T_o	0.59	0.60	0.61	0.61	0.62	0.63	0.64	0.65	0.66	0.67

Since alpha is not sensitive to Z, the estimate of $Z = 0.5$ in this report is a safe basis for calculating alpha. Similarly, the calculated analysis of liquids based upon the analysis of hydrogen liberated by calcium will be affected very little even if the extent of reaction differs somewhat from the 50 per cent of completion found in this work.

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