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DETERMINATION OF THE OVERALL DISTRIBUTION CONSTANT OF DEUTERIUM IN THE GS PROCESS FOR HEAVY WATER PRODUCTION

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ABSTRACT

The overall distribution constant β of deuterium between mutually saturated phases of water and hydrogen sulfide has been experimentally determined as a function of temperature. The measurements were made with a teflon-sealed stainless steel exchange chamber of 500 ml capacity. At a total pressure of 20 kg/cm^2, the experimentally determined values of β were 2.335, 2.260, 1.650, and 1.586 at 30, 35, 130, and 135°C, respectively. These results are in good agreement with the corresponding calculated values.

INTRODUCTION

In the well known Girdler-Sulfide or Girdler-Spevack process which has held a pre-eminent position in the production of heavy water (1), the overall distribution constant β of deuterium between the mutually saturated phases of liquid water and gaseous hydrogen sulfide is of primary importance in plant design. At low deuterium concentrations, the distribution constant can be expressed (2) in the form

$$\beta = \frac{(1 + H)(S + K_x)}{\alpha(1 + S)(1 + HK_x)} , \tag{1}$$

where H denotes the mols of water vapor per mol of gas in the gas phase, S is mols of sulfide gas per mol of water, dissolved in the liquid phase, α is the relative volatility of HDS compared with H_2S, and is assumed to be equal to the relative volatility of HDO compared with H_2O, and $K_x = [HDO]_\ell/[HDS]_g$ is the ratio of the indicated deuterated species in the liquid and gaseous phases. The present study is directed toward the experimental determination of the constant β as the ratio of $[D]_\ell/[D]_g$.

EXPERIMENTAL

Apparatus and Materials

A sketch of the all-stainless steel apparatus is depicted in Fig. 1. It consists of three major components. The first of these is a 500-ml exchange chamber (Chamber A). It is connected through a valve to the second component, which is a gas sampling chamber (Chamber B) of about the same capacity. The gas sampling chamber can be connected to the H_2S generation system and can also serve as a reservoir for H_2S when the gas is chilled with a dry ice bath.

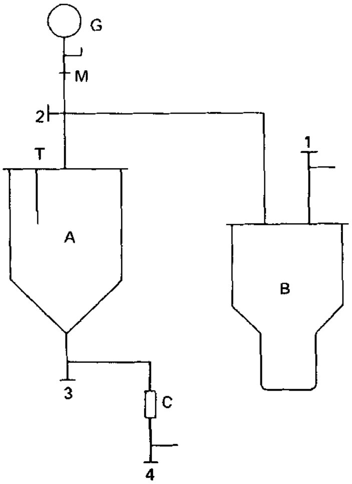

FIGURE 1. Sketch of the apparatus. A, exchange chamber; B, gas sampling chamber; C, liquid sampling chamber; T, thermometer sheath; G, pressure gauge; M, teflon membrane; 1,2,3,4, needle valves with teflon gaskets.

The bottom of the exchange chamber leads through a valve to the third component, a liquid sampling chamber (Chamber C) of 3-ml capacity. The exchange chamber is provided with a pressure gauge which is protected from attack by H_2S through the use of paraffin oil and a teflon membrane. The gauge is calibrated, and yields pressure values accurate to within 0.2 kg/cm^2. The exchange chamber is thermostated to maintain a set temperature to within $\pm 0.1°C$. The apparatus was tested before service and can operate at a pressure of 30 kg/cm^2 at 200°C.

The dilute heavy water which was used contained about 1.5 atom % D. Precise pycnometry yielded results accurate to within ± 0.01 atom % D, while comparative measurements, with a float, resulted in values which were accurate to within ± 2 ppm D. The H_2S gas, which was prepared from Na_2S, was 98.6% pure; the main impurity was CO_2.

Procedure

When the apparatus is ready for use, valve 3 (see Fig. 1) is closed, the thermometer sheath is screwed off, and 30 ml of dilute heavy water is admitted by syringe. (This amount suffices for six or seven successive determinations.) The thermometer sheath is then screwed on again. In order to prevent loss of water through evaporation, chambers A and B are first evacuated to 100 torr, and H_2S admitted to bring the pressure back to 760 torr. Such a procedure is repeated until the partial pressure of air becomes less than 10 torr. Thus the residual air contributes only about 0.05% impurity to the H_2S gas at a pressure of 20 kg/cm^2.

Valve 2 is then closed, and chamber A heated to the required temperature. At the same time, H_2S is transported through valve 1 into chamber B, where it is condensed by means of a dry ice bath. Collection of about 1 mol of H_2S usually requires about 20 min. Thereafter, valve 1 is closed, the cooling bath removed, chamber B warmed up with a water bath, and the H_2S introduced into chamber A through valve 2. When the required temperature and pressure are attained, valve 2 is closed and the H_2S in chamber B removed and absorbed into a solution of Na_2S for later use.

The establishment of isotopic exchange equilibrium requires about five hours. During this time, sampling chambers B and C are evacuated to ensure dryness, and two electric furnaces in a gas handling train are brought to temperature. One of these furnaces surrounds a porcelain tube which contains Cu for the conversion of H_2S into hydrogen; the hydrogen so produced is subsequently converted to water in a CuO bed which is contained in the second furnace. The Cu bed is maintained at 700°C when in use, and the CuO bed is held at 650°C.

A 3-ml liquid sample is taken first; during sampling the pressure decreases by only 0.1 to 0.2 kg/cm^2. In contrast, withdrawing a 500-ml volume of the gas phase results in a pressure drop of about 7 kg/cm^2 at 30 to 35°C, and about 10 kg/cm^2 at 130 to 135°C. Gas sampling is therefore completed within a 5 to 10 sec time period so as not to perturb the state of equilibrium appreciably. An approximately equal amount of H_2S is later admitted into chamber A from chamber B, as described above, for the next experiment.

Analysis

The liquid sample is first degassed with the aid of an ice-salt bath. The trace of dissolved H_2S in the water is oxidized by adding a few crystals of $KMnO_4$ until the pink color persists. After BaO is added, to render the water alkaline, a two-stage vacuum distillation is performed until the aqueous sample indicates a specific conductance of 2×10^{-6} $ohm^{-1} cm^{-1}$. The H_2S from the degassing operation is converted by Cu and CuO into water, which is then similarly purified. These two portions of water are weighed separately, before being combined in the vacuum still. This total, Water-L, represents the liquid phase insofar as the deuterium concentration is concerned.

On the other hand, the gas sample is first passed through a trap that is cooled with an ice-salt mixture to condense the water vapor. The gas is then transported through the Cu and CuO beds to convert the hydrogen in the H_2S to water. The two portions of water are subsequently purified, weighed separately, and combined in the vacuum still. This water, Water-G, represents the gas phase in exchange equilibrium as regards the deuterium content.

Both Water-L and Water-G are then analyzed by the temperature-pressure float method, which is a modification of the temperature float method described previously (3). A cylindrical vitrous quartz float, 15-mm tall and with tapered ends, is situated in a 2.5-ml borosilicate glass chamber. The bottom of this chamber is conical, to permit alignment of the float. The top of the chamber has an extension which serves as the body of the flotation tube. The chamber is closed by a ground glass stopper which carries a capillary tubing that is directed upward to accommodate the expansion of water. After degassing the sample, air will re-enter the tube, but it cannot diffuse into the chamber during measurement.

In the temperature-pressure float method, the pressure coefficient of flotation temperature, expressed in °C/torr, is first determined for a certain float with its density suitable to the range of deuterium concentrations of interest. With the help of this coefficient, the flotation temperature of a certain water sample can be converted into the normal flotation temperature, that is, at 760 torr, by applying a correction for the pressure difference between the observed and the normal. This method is rapid, since only a few minutes are required to adjust a pressure, and usually three different pressures, corresponding to three different rising or falling velocities of the float, can fix the flotation pressure. On the other hand, adjusting a thermostat temperature would require at least half an hour.

In actual practice, Water-L and Water-G are compared with a standard water sample. Of course, a correction for the Dole effect (4) should be applied to the amount of water obtained from the CuO combustion. From the thermal expansion coefficients of light and heavy water, and from the normal flotation temperatures, the density differences can be determined. These differences, in turn, can be converted into deuterium concentration differences. By using a bath that is thermostated to within ±0.001°C and a mercury manometer of 6 mm bore, an accuracy of ±0.2 µg/ml in density difference can be readily attained by this method.

RESULTS

Eleven measurements were made at about 30°C, and nine at temperatures of about 35°C. Actually, the temperatures observed ranged from 29.8 to 35.2°C, and the pressures ranged from 17.6 to 20.9 kg/cm^2 (with one exception of 15.6 kg/cm^2). These 20 sets of data yield, by means of graphic analysis, values of β at 30 and 35°C and at 18 and 20 kg/cm^2 pressure.

Five measurements were made at about 130°C, and ten at temperatures of about 135°C. The actual temperatures ranged from 130 to 135.5°C, while the pressures ranged between 19.2 and 20.8 kg/cm^2 (with one exception of 17.7 kg/cm^2). Similar graphic treatment of these 15 sets of data yielded values of β for 130 and 135°C at 20 kg/cm^2.

The final results are presented in Table 1 and are compared with previously calculated values (5). The agreement between the two sets of results is excellent.

Table 1. Comparison of observed and calculated β values

T, °C	30	30	35	35	130	135
P, kg/cm^2	18	20	18	20	20	20
β(obs.)	2.29_2	2.33_5	2.27_2	2.26_0	1.65_0	1.58_6
β(calc.)	2.29_3	2.28_9	2.25_8	2.25_4	1.62_3	1.58_4

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