A Determination of the Equilibrium Constant of HTO-H_2S Reaction

A Determination of the Equilibrium Constant of HTO-H_2S Reaction*

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Synopsis

The equilibrium constants of the chemical exchange reaction between HTO and H_2S are determined at 1 atm to enrich tritiated water. The separation factor of one stage is defined, and it is increasing with the increase of temperature in the batch method. For the first step to make a practical application of the chemical exchange reaction to enrich tritium, the H_2S gas circulation method is investigated.

I. Introduction

Most of tritium existed in the environment have been produced by the nuclear reaction of cosmic ray with ^{14}N, $^{14}N(n,T)^{12}C$, and by the thermonuclear detonation that has been testing for 30 years.[1] Tritium released from the nuclear power plants and the fuel reprocessing factories are in a minality now, but are increasing gradually. Most of tritium exist as a tritiated water. The released tritium causes the problems of not only the radioactivity polution but also no utility of energy. One of the most practicable way to prevent tritium from releasing is to enrich tritiated water, that makes the volume of the tritiated water decrease, and to store it.

The enrichment of tritium is based on the same principle of the enrichment of deuterium. One of the most widely used way to enrich deuterium is the dual-temperature chemical exchange reaction of D_2O-H_2S(GS method). Lin[2] determined the equilibrium constants of HTO-H_2S reactions at about 19 atm, at that pressure the deuterium plants are operating.

In this work, we try to determine the dependency of the equilib-

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rium constant of HTO-H_2S reaction on temperature at 1 atm in detail. First, the constants were determined by the batch method, then by the H_2S gas circulation method.

II. Experimental

1. Batch method

The apparatus of the batch method is shown in Fig.1. This is constituted mainly three parts: the reaction vessel, the reservoir of HTO, and the gas-filling-up instrument which involves oil and mercury manometers. All of them are made of Pyrex glass.

Three milliliters of HTO(∿0.3 μCi/ml), which was obtained from New England Nuclear Corp. and diluted with distillated water to make a stock solution, was taken into the reservoir, which was fitted to the reaction vessel. Then, HTO was freezed by the liquid air.

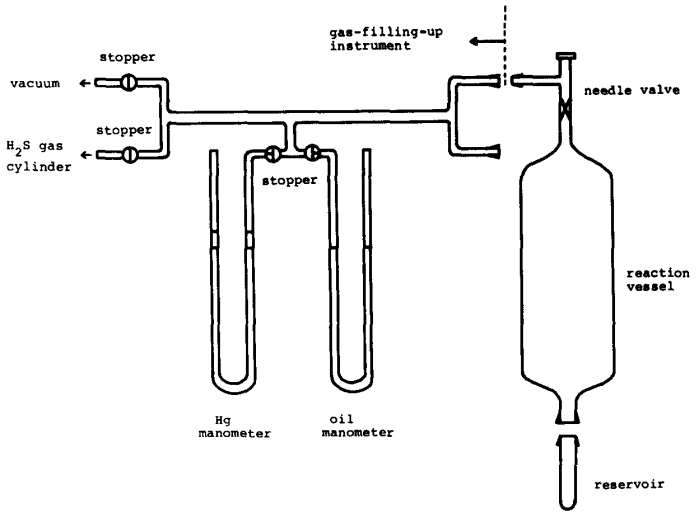

Fig.1. Experimental apparatus of batch method

The reaction vessel and the reservoir were fitted to the gas-filling-up instrument, and were made vacuous by the rotary vacuum pump. Then H_2S gas(>99% purity) was introduced into them untill the pressure is equivalent to the atmoshpere, that was checked by the manometers.

After shutting the stoppers and freezed HTO was resolved perfectly, the reaction vessel and the reservoir were separated from the gas-filling-up instrument, and fitted to the shaker horizontally, then were shaking about 120 minutes in a thermostatic air-bath (Ônishi Netsugaku Kogyo Co.,Ltd. ; ±1°C). It is confirmed that equilibrium was achieved enough in 120 minutes by a preliminary experiment.

After shaking, the reservoir was separated from the reaction vessel, and 1 ml of HTO was taken into the scintillation vial to determine the radioactivity by the liquid scintillation counter (Packard 3350). The radioactivity of the stock solution was also determined.

The equilibrium constants of the reaction were examined in a temperature region of 0-60°C, and the dependency of the equilibrium constant on temperature was determined.

2. Gas circulation method

The H_2S gas circulation method was investigated for the first step to make a practical application of the dual-temperature chemical exchange reaction.

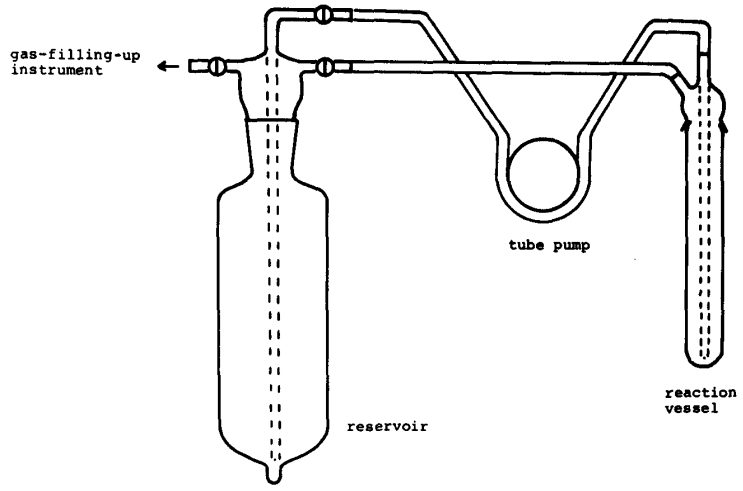

Fig.2. Experimental apparatus of gas circulation method

The apparatus was shown in Fig.2. This involves mainly three parts: gas reservoir(3250 ml), tube pump(TOKYO RIKAKIKAI CO.,LTD. RP-10), and reaction vessel(75 ml). For conecting the parts and for using it in the tube pump, IUCHI CHEMITUBE was selected, which had been the most durable to H_2S in available tubes by the preliminary examination.

Five milliliters of HTO(∿0.3 μCi/ml) was taken into the reaction vessel. After freezing HTO, the reaction vessel and the gas reservoir were jointed to the gas-filling-up instrument which was shown in Fig.1, and filled with H_2S gas in the same way as mentioned in the batch method. The reaction vessel and the reservoir were placed in the thermostatic air-bath, and H_2S gas was circulated at 100 ml/min by the tube pump for 4 hours. Then, the radioactivities of HTO after and before the circulation were determined.

III. Results and Discussion

The reaction of HTO-H_2S system and its constant are written as

follows:

$$H_2S(g) + HTO(l) \overset{K}{=} HTS(g) + H_2O(l) \quad \text{-------(1)}$$

$$K = [HTS]_g[H_2O]_l/[H_2S]_g[HTO]_l \quad \text{----------(2)}$$

where, g in parentheses and subscript g represent the gas phase, and l the liquid phase.

Generally, the separation factor of one stage of the chemical exchange reaction(α_s) is defined as:

$$\alpha_s = \frac{[T]_g/[H]_g}{[T]_l/[H]_l} \quad \text{-------(3).}$$

This can be represented in all species to be existed.

$$\alpha_s = \frac{2[T_2S]_g + [HTS]_g + [HTO]_g + 2[T_2O]_g}{2[H_2S]_g + [HTS]_g + [HTO]_g + 2[H_2O]_g} \times \frac{2[H_2O]_l + [HTO]_l + [HTS]_l + 2[H_2S]_l}{2[T_2O]_l + [HTO]_l + [HTS]_l + 2[T_2S]_l} \quad \text{----(4)}$$

In this equation, the molecules which are composed of two tritium atoms are neglected except in a case of high concentration of tritium. And the following relations are found in each phases;
$[H_2O] \gg [HTO]$, $[H_2S] \gg [HTS]$, $[H_2O] \gg [HTS]$, $[H_2S] \gg [HTO]$.
Moreover, H_2S gas dissolved in water is negligible, so we can say;
$[HTO]_l \gg [HTS]_l$, $[H_2O]_l \gg [H_2S]_l$. Therefore, α_s is represented

$$\alpha_s = \frac{[HTS]_g + [HTO]_g}{[H_2S]_g + [H_2O]_g} \times \frac{[H_2O]_l}{[HTO]_l} \quad \text{--------(5).}$$

The contribution of $[HTO]_g$ and $[H_2O]_g$ are negligible in a low temperature, but are large in a high temperature at 1 atm. Practical deuterium plants are operating at more 10 atm, so $[HTO]_g$ and $[H_2O]_g$ are relatively lowered and negligible.

Let a new separation factor (α_s') define.

$$\alpha_s' = \frac{(T/H) \text{ in } H_2S}{(T/H) \text{ in } H_2O} \quad \text{-----(6)}$$

This is rewritten in the same analysis of α_s.

$$\alpha_s' = \frac{[HTS]_g}{[H_2S]_g} \times \frac{[H_2O]_l + [H_2O]_g}{[HTO]_l + [HTO]_g} \quad \text{------(7)}$$

where, in the second term,

$$\frac{[H_2O]_l}{[HTO]_l} \simeq \frac{[H_2O]_g}{[HTO]_g} \quad \text{-----(8).}$$

So, the equation (7) is to be equal to equation (2). The value of $[HTO]_l$ is obtained by determining the radioactivity. The other values are obtained by subtructing $[HTO]_l$ from the concentration of tritium in initial tritiated water, and from the equivalent values of the vapor pressure of H_2O and the solubility of H_2S in H_2O at each temperature.

The results obtained by the batch method are shown in Fig.3. The broken line shows the values obtained from Lin's data.[2] The values of α_s and α_s' are increasing with the increase of the temperature. The value of α_s is more increasing than α_s' due to the vapor pressure of water. The values of α_s' is agreed well with the values obtained from Lin's data. So, α_s' indicates the practical values which may be obtained in the practical enrichment of tritium at high pressure, namely α_s' is independent of pressure.

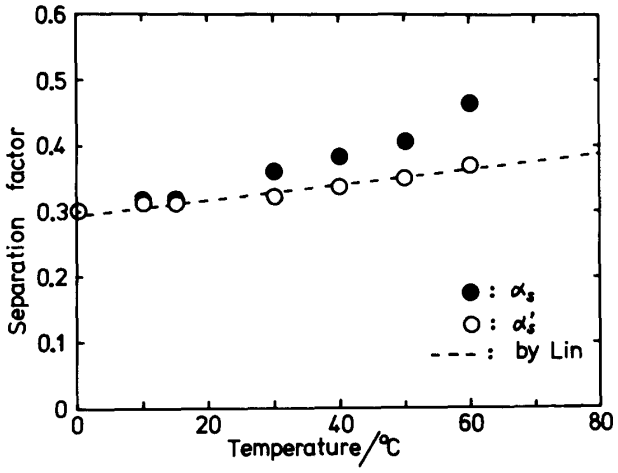

Fig.3. Dependency of separation factor of batch method on temperature.

The results of the gas circulation method which is the first step for enrichment of tritium are shown in Fig.4. The values of α_s and α_s' are both slightly increasing with the increase of the temperature, but are lower than those of the batch method. This may be caused by tritium released from the system through the CHEMITUBE which is slightly corroded by H_2S gas at the

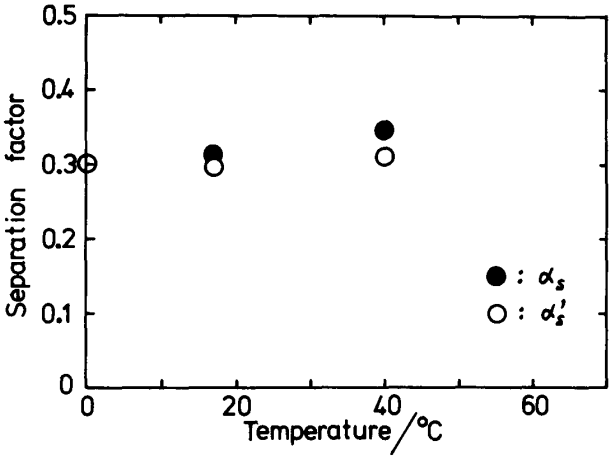

Fig.4. Dependency of separation factor of gas circulation method on temperature.

pressed part in the tube pump. So, the other circulation systems are to be examined.

Acknowledgement

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References

(1). D. G. Jacobs, TID-24635(1968).
(2). K. H. Lin, ORNL-TM-3976(1972).