Enrichment of Tritium by Diffusion through Palladium

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The different diffusion velocities of Hydrogen and Tritium through Palladium open the possibilities of Tritium enrichment in the residual gas mixture. The relative diffusion velocity of Tritium versus temperature and the enrichment related to the initial and final quantities of the mixture as well as the diffusion temperature are described.

The diffusion of Hydrogen through Palladium and other metals is well known[1]. In particular, for Palladium, curves are given for the diffusion velocity of Hydrogen as a function of temperature, pressure and thickness[2] of the Palladium. From Richardson's equation, the diffusion velocity is defined by:

$$V = C\,P^{1/2}\,T^{1/2} \exp\{-E/(R\,T)\} \tag{1}$$

where P is the gas pressure, T the absolute temperature and E the dissociation energy for the particular gas. C is dependent on the thickness of the Palladium. Considering the two Hydrogen isotopes H^1 and H^3, the ratio of their diffusion velocity can be written as:

$$V_3/V_1 = (C_3/C_1) \exp\{-(E_3 - E_1)/(R\,T)\} \tag{2}$$

where subscripts 3 and 1 refer to H^3 and H^1 respectively. The expression (2) increases with temperature if $E_3 > E_1$. In reality, as it will be seen, this has been found in the measurements described hereafter, as the ratio V_3/V_1 at 450 °C is twice the corresponding ratio at 180 °C.

The measurements were carried out in order to test the conditions for a complete separation of the Hydrogen isotopes from other gases by diffusion through Palladium. This method has been applied in our laboratory and others, for the separation of small quantities of Tritium from meteorites[3] and from irradiated samples[4]. On the other hand, it was interesting to study the Tritium enrichment by this diffusion mechanism.

I. The Method

In the diffusion measurements, Hydrogen-Tritium mixtures with a Tritium concentration of about 10^{-11} have been used. The Hydrogen has been measured volumetrically, the Tritium by its β activity. For the β activity determination, the mixture was filled into a cylindrical Geiger-Müller counter.

Two series of measurements have been carried out. In the first, the initial Hydrogen and Tritium mixture has been kept constant, and the activity of the diffused gas mixture measured at different temperatures, keeping the total amount of diffused gas approximately constant. In this way, only a very small amount of the total gas diffused through the Palladium. In the second type of measurement, only a very small fraction of the initial gas was left undiffused. The Tritium concentration of this residual gas fraction has been measured and the Tritium enrichment in this fraction determined as a function of the Palladium temperature.

II. The Apparatus

Figure 1 shows the general scheme of the diffusion apparatus. The Palladium diffusion tube is shown in detail in Figure 2. During the diffusion, the Palladium temperature was kept constant within about 5%. On the downstream side (right side in Fig. 1) of the Palladium diffusion tube the pressure was maintained at 10^{-4} torr, using a mercury diffusion pump. The diffused Hydrogen was pumped into a Geiger-Müller counter by means of an automatically operated Toepler pump. On the upstream side of the Palladium a large volume (10 litres) of H^3 and H^1 mixture of 220 torr ensured that the initial condition for the gas mixture could be kept constant, as only 6 torr·litre were necessary for

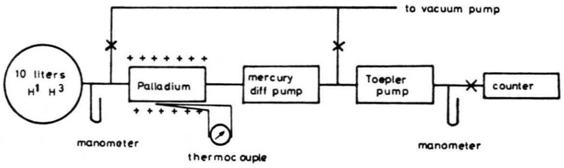

Fig. 1. Block diagram of the diffusion apparatus.

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[1] For a full list of references see R. Barrer, Diffusion in and through Solids, Cambridge University Press, 1951.

[2] C. Bachman and P. Silberg, J. Chem. Phys. **29**, 777 [1958].

[3] e. g. K. Goebel and P. Schmidlin, The Radiation Age of Meteorites. Proc. Conf. on Radioisotopes in the Physical Sciences and Industry, Copenhagen Sept. 1961, Intern. Atomic Energy Agency, Vienna 1962.

[4] e. g. E. Fireman and J. Zähringer, Phys. Rev. **107**, 1695 [1957].

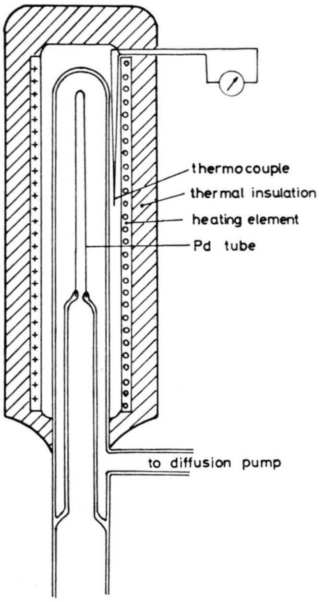

Fig. 2. The Palladium tube with furnace.

one measurement. The specific activity of the initial mixture was 0.13 dpm/torr·ml. For the activity measurements, a cylindrical Geiger-Müller counter (wall material Kovar 0.5 mm thick, counter 30 mm ⌀ and 210 mm length) was used with a 0.09 mm stainless steel centre wire and a filling of 110 torr self-quenching gas (55% Argon and 45% C_2H_4).

A plateau of 300 V length and less than 3% slope was obtained. The counting rate was determined by using an anticoincidence system for obtaining a lower counting background. Depending on the diffusion velocity, the actual counting rates ranged from some 100 up to 3000 cpm. The background was about 2.5 cpm.

III. Results

1. *Diffusion Velocity of Hydrogen and Tritium*

Figure 3 shows the dependence of the diffusion velocity of Tritium on temperature. In another series of measurements, the dependence of the diffusion velocity on the pressure has been found to agree with the $\sqrt{P}$ law (Richardson's equation). The counting rate of the Tritium for the diffused gas mixture has been measured as a function of the temperature. In Fig. 4, the results show that the diffusion velocity of Tritium relative to that of Hydrogen rises rapidly between 200 and 300 °C. At higher temperature (450°) the relative diffusion speed is about twice that for 100 °C. This dependence has been measured at a Hydrogen pressure of 180 torr. However, tests have shown that this behaviour to a first approximation is independent of the Hydrogen pressure.

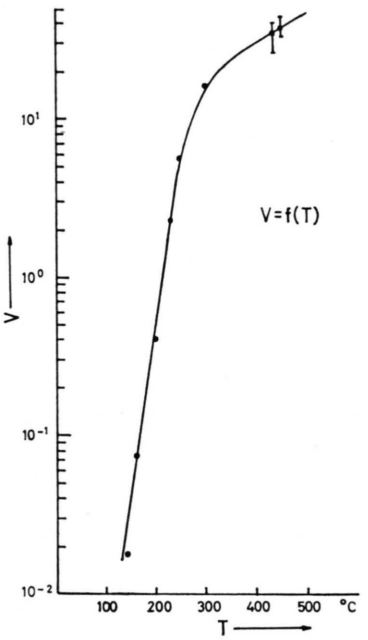

Fig. 3. The diffusion velocity *V*, in arbitrary units, versus temperature.

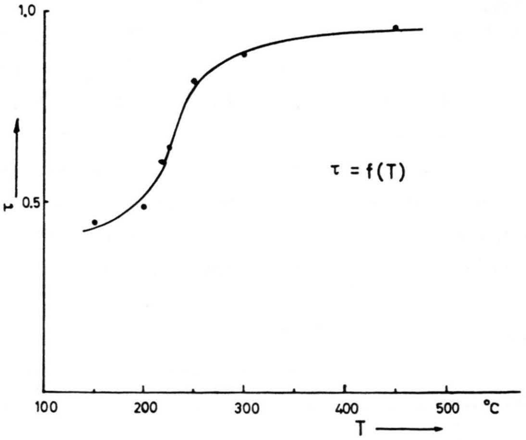

Fig. 4. The relative diffusion velocity Tritium/Hydrogen as function of temperature.

2. *Tritium Enrichment*

The fact that the diffusion speed of H^1 is greater than that for Tritium in Palladium, suggests the use of this phenomenon for a Tritium enrichment in a Tritium-Hydrogen mixture. From the curve in Fig. 4 it can be derived that this enrichment is probably highest at low temperatures of the Palladium. Quantitatively we get the enrichment if we use the formula

$$\tau/\tau_0 = (Q_0/Q)^{1-1/\varepsilon}$$

(see Appendix) by measuring the parameter ε. In this formula τ and τ_0 stand for specific activity, whereas Q_0 is the initial quantity of Hydrogen and Q the quantity of Hydrogen which did not diffuse. In our measurement ε was determined by taking Q_0/Q in the order of 200. In Fig. 5, ε is given as a function of the temperature. By repeating our measurements at different initial concentrations, it has been found that ε is independent of the initial concentration of Tritium.

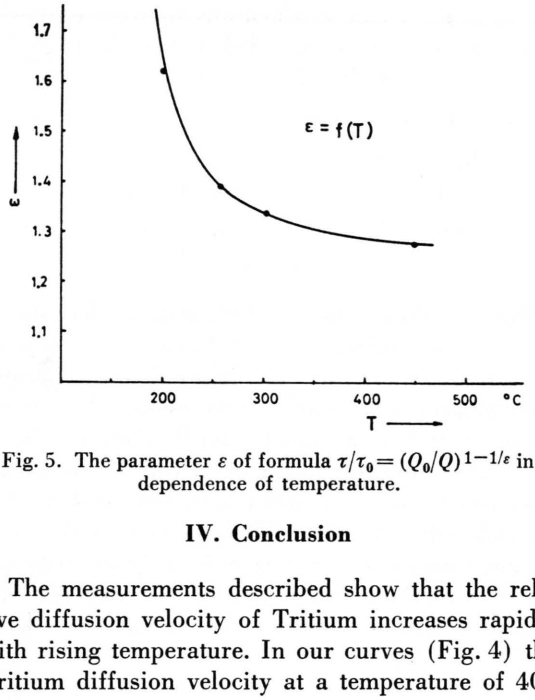

Fig. 5. The parameter ε of formula $\tau/\tau_0 = (Q_0/Q)^{1-1/\varepsilon}$ in dependence of temperature.

IV. Conclusion

The measurements described show that the relative diffusion velocity of Tritium increases rapidly with rising temperature. In our curves (Fig. 4) the Tritium diffusion velocity at a temperature of 400 °C is nearly the same as the diffusion velocity of Hydrogen. For obtaining complete separation of Hydrogen as well as Tritium from any other gas it is desirable to work at Palladium temperatures higher than 300 °C.

The different diffusion velocities of Tritium and Hydrogen through Palladium at appropriate temperatures offer the possibility of Tritium enrichment. However, only at temperatures where the absolute diffusion velocities are small (below ~150 °C), a significant enrichment of Tritium can be obtained. For large quantities it is therefore preferable to use electrolytical enrichment, but for small quantities of Hydrogen (corresponding to $<0.5\ \text{cm}^3$ of water) where electrolytical methods are technically complicated, the enrichment of Tritium by diffusion through or adsorption on [5] Palladium is simpler.

Appendix

If p and t represent the number of molecule of H^1 and H^3, in the time interval $\mathrm{d}x$ the quantities $\mathrm{d}p$ and $\mathrm{d}t$ might diffuse through the Palladium at the absolute temperature T. The parameter ε gives the ratio between relative quantities of p and t which diffused in the time interval $\mathrm{d}x$.

$$\mathrm{d}p/p = \varepsilon \cdot \mathrm{d}t/t\,. \qquad \text{(A.1)}$$

If ε is independent of the concentration, the integration of (A.1) gives

$$p = (t/t_0)^{\varepsilon}\,. \qquad \text{(A.2)}$$

The subscript 0 represents the initial quantities of p and t. If Q represents the total quantity of Hydrogen-Tritium mixture, for small concentrations of Tritium, we have $Q = p$. With this we get

$$Q/Q_0 = p/p_0 = (t/t_0)^{\varepsilon} \qquad \text{(A.3)}$$

and if we put $\tau = t/p$, it follows that

$$\tau/\tau_0 = (Q_0/Q)^{1-1/\varepsilon} = R/R_0\,, \qquad \text{(A.4)}$$

R = relative Tritium activity in the gas mixture (measured, for example, in dpm/torr·ml).

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[5] E. Glueckauf and G. P. Kitt, in J. Kistemaker, J. Bigeleisen and A. O. Nils (editors), Proc. Intern. Sympos. Isotope Separation, Amsterdam 1958.