Enrichment of Tritium by Diffusion through Palladium

S. Charalambus and K. Goebel
CERN–European Organization for Nuclear Research, Geneva

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. In particular, for Palladium, curves are given for the diffusion velocity of Hydrogen as a function of temperature, pressure and thickness of the Palladium. From Richardson’s equation, the diffusion velocity is defined by:

$$V = C P^{1/3} T^{1/3} \exp\left\{-E/(RT)\right\}$$  \hspace{1cm} (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:

$$\frac{V_3}{V_1} = \left(\frac{C_3}{C_1}\right) \exp\left\{-\left(\frac{E_3 - E_1}{1/(RT)}\right)\right\}$$  \hspace{1cm} (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 and from irradiated samples. On the other hand, it was interesting to study the Tritium enrichment by this diffusion mechanism.

---

1. For a full list of references see R. Barber, Diffusion in and through Solids, Cambridge University Press, 1951.
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 φ 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 \( V/P \) 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 Hydro-

gen rises rapidly between 200 and 300 °C. At higher temperature (450°C) 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.

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

\[ \frac{\tau}{\tau_0} = \left( \frac{Q_0}{Q} \right)^{1 - 1/\varepsilon} \]

(see Appendix) by measuring the parameter \( \varepsilon \). In this formula \( \tau \) and \( \tau_0 \) 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 \( \varepsilon \) was determined by taking \( Q_0/Q \) in the order of 200. In Fig. 5, \( \varepsilon \) is given as a function of the temperature. By repeating our measurements at different initial concentrations, it has been found that \( \varepsilon \) is independent of the initial concentration of Tritium.

\[ \text{Fig. 5. The parameter } \varepsilon \text{ of formula } \frac{\tau}{\tau_0} = \left( \frac{Q_0}{Q} \right)^{1 - 1/\varepsilon} \text{ in dependence of temperature.} \]

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 \( \sim 150^\circ \text{C} \)), 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 \( \text{H}^1 \) and \( \text{H}^3 \), in the time interval \( dx \) the quantities \( dp \) and \( dt \) might diffuse through the Palladium at the absolute temperature \( T \). The parameter \( \varepsilon \) gives the ratio between relative quantities of \( p \) and \( t \) which diffused in the time interval \( dx \).

\[ \frac{dp}{p} = \varepsilon \cdot \frac{dt}{t}. \quad \text{(A.1)} \]

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

\[ p = \left( \frac{t}{t_0} \right)^{\varepsilon}. \quad \text{(A.2)} \]

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

\[ \frac{Q}{Q_0} = \frac{p}{p_0} = \left( \frac{t}{t_0} \right)^{\varepsilon} \quad \text{(A.3)} \]

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

\[ \frac{\tau}{\tau_0} = \left( \frac{Q_0}{Q} \right)^{1 - 1/\varepsilon} = R/R_0, \quad \text{(A.4)} \]

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