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THE DIFFUSIVITY OF HYDROGEN ISOTOPES IN LIQUID
LITHIUM AND IN SOLID YTTRIUM

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THE DIFFUSIVITY OF HYDROGEN ISOTOPES IN LIQUID
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ABSTRACT

The separation of tritium from liquid lithium at low concentrations is an important problem for fusion technology. One of the most promising techniques for effecting this separation involves sorbing the tritium on solid yttrium metal. Reliable diffusivity data are essential for a realistic evaluation of this technique.

This paper reviews the bodies of relevant experimental diffusivity data, i.e., data on protium diffusion in liquid lithium, protium diffusion in solid yttrium, and the isotope effect in metals. On the basis of these data and in the light of standard correlations, the following equations are proposed for the diffusivity of tritium in liquid lithium and in solid yttrium respectively:

$$\log_{10} D_{T-Li} = -9.038 + 1.737 \log_{10} T - 110/T \text{ cm}^2/\text{s},$$

and

$$\log_{10} D_{T-Y} = -2.391 - 2558/T.$$

These equations show that the geometries of yttrium systems for tritium gettering in fusion reactors are of quite practicable dimensions.

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I. SCOPE

It is generally assumed that the first fusion power reactors will use deuterium and tritium as the principal fuels and that the tritium will have to be bred by capturing neutrons from the fusion reaction in a blanket containing lithium in some form. The bred tritium must then be separated from the blanket material and introduced into the fusion reactor fuel mix.

As demonstrated by Buxbaum and Johnson (1980), from many standpoints, the simplest and most attractive breeding medium is liquid lithium, and the most attractive tritium recovery medium is solid yttrium metal. However, in the absence of experimental data on test loops, the practicability of this separation system can be gauged only from paper studies, and such studies will be critically dependent on reliable information on the relevant diffusivity properties. This paper presents the best available information on these properties.

II. THE DIFFUSIVITY OF TRITIUM IN LIQUID LITHIUM

Cussler (1976) has generalized that the diffusivity of any solute in any liquid solvent is a constant approximating $0.7 \times 10^{-5} \text{ cm}^2/\text{s}$. While this assertion tends to be accurate within an order of magnitude, a more reliable estimate, polymeric liquids excepted, may be made on the basis of the Nernst-Einstein (Langevin, 1908) equation. A convenient simplification of this equation is the Stokes-Einstein equation (Einstein, 1905) viz.,

$$D = kT/6\pi\bar{r}\mu \quad (1)$$

where k is Boltzman's constant, 1.3805×10^{-13} N-cm/K; T is absolute temperature, K; μ is the solvent viscosity, N-s/cm²; and $\bar{r}$ is the effective radius of the diffusing species cm. For relatively spherical molecules,

$$\bar{r} \approx (3V/4\pi N_{AV})^{1/3} \quad (2)$$

where V is the molecular volume at the normal boiling point, cm³/g mol; and N_{AV} is Avogadro's number, 6.02×10^{23} molecules/g mol. For nonspherical molecules, the effective radii may be determined from their pseudo-steady hydrodynamic mobilities (Brenner, 1974).

The effective radius of the lithium hydride molecule, when calculated by Eq. (2), is found to be 1.7 Å. This radius, when inserted into Eq. (1), does not correlate well with the experiment, presumably because the diffusing species is not the lithium hydride molecule. Rather hydrogen diffuses in liquid lithium as Li₂H molecules, Li₃H molecules, or possibly as larger conglomerates.

For smaller molecules diffusing in non-polymeric liquids, the most often used correlations are those of Wilke and Chang (1955) and Scheibel (1954). Their correlations may be expressed as

$$D = 7.4 \times 10^{-8} \frac{(M_B)^{1/2} T}{\mu^{0.6} V_a^{0.6}} \quad (3)$$

and

$$D = 8.2 \times 10^{-8} \frac{T}{\mu^*} \frac{1 + \frac{3V_B}{V_A}^{2/3}}{(V_A)^{1/3}}, \quad (4)$$

respectively. Here V_A and V_B are the molecular volumes of the solute and the solvent respectively, cm^3/mole ; M_B is the solvent's molecular weight, g/mol ; T is absolute temperature, K ; and μ^* is the solvent viscosity in centipoise. The experimental data in both of these references are seen to support the assertion from theoretical calculations (e.g., Batchelor, 1976) that liquid diffusivity is proportional to absolute temperature divided by viscosity, poise, and

$$D = \frac{aT}{\mu} \quad (5)$$

where a is a constant determined by temperature-independent properties of the solute-solvent pair.

Equation 5, which has been found to be universally applicable to nonpolymer systems, can be used to extrapolate the available, high-temperature protium-lithium diffusivity data into the low-temperature regime. Furthermore, since molecular volume is largely independent of isotope mass, Eqs. (1), (3), and (4) each predict that the constant, a , in Eq. (5) is isotope independent. Thus, at any given temperature, the diffusivity of all isotopes of hydrogen in liquid lithium should be the same.

We are now in a position to fit experimental data to Eq. (5). The viscosity of liquid is reliably reported by Shpil'rain et al. (1965), over the range 185 to 1000°C, as

$$\log_{10} \mu^* = 1.4936 - 0.7368 \log_{10} T + 109.95/T. \quad (6)$$

It is not expected that the lithium viscosity is affected by small hydrogen concentrations. Equations (5) and (6), when fitted with Alire's (1976) high-temperature, lithium-protium diffusion data (Table 1), produce a broad range diffusivity correlation applicable to all hydrogen isotopes. The value of a is found to be 2.86×10^{-10} erg/cmK with a standard deviation of 18%. The diffusivity of hydrogen isotopes in liquid lithium thus calculated is

$$\log_{10}(D \pm 18\%) = -9.038 + 1.737 \log_{10} T - 110/T. \quad (7)$$

While Eq. (7), strictly speaking, is only applicable to the diffusion of hydrogen isotopes in pure lithium, it may be used as an aid in predicting the diffusivity of hydrogen isotopes in molten lithium-rich alloys of interest to fusion technology: lithium-lead and lithium-aluminum. An equivalent radius or volume for the diffusing lithium hydride species may be calculated by combining Eqs. (7) and (6) with Eq. (1), (3), or (4). For example, $\bar{r}$ as calculated from Eqs. (7), (6), and (1), is 2.65 Å. Given this value, assumed constant for lithium-rich systems, and a viscosity relation for the molten alloy in question, the calculation of the diffusivity of hydrogen isotopes in that alloy is straightforward.

Table 1: Diffusion Coefficients of H_2 in Lithium at
High Temperatures, from Alire (1976).

Temperature (°C)	Pressure (Pa)	Diffusion Coefficient (cm^2/s)
800	575.0	0.97×10^{-4}
800	15.6	1.10×10^{-4}
800	15.6	0.95×10^{-4}
800	1097.	1.11×10^{-4}
800	1097.	1.04×10^{-4}
800	1097.	1.33×10^{-4}
800	1097.	1.25×10^{-4}
800	1097.	1.30×10^{-4}
805	575.	1.33×10^{-4}
855	575.	1.54×10^{-4}
905	575.	2.85×10^{-4}

III. THE DIFFUSIVITY OF HYDROGEN ISOTOPES IN YTTRIUM

The full body of experimental data for low concentration hydrogen diffusion in yttrium metal is presented in Fig. 1. While we expect that hydrogen diffuses through hexagonal-close-packed yttrium metal by an interstitial mechanism, this assumption leads to the prediction of an Arrhenius' law temperature-dependence for diffusion. The data in Fig. 1 do not immediately support this expectation.

The most striking feature of Fig. 1 is the fact that those values of the diffusivity coefficient which were measured by the rate of observed vacuum desorption, Voroboyov et al. (1976) and Talbot et al. (1979), are much lower than those values of the diffusion coefficient measured by neutron scattering or quantitative analysis. The simplest explanation for this discrepancy is that surface resistance, the hydrogen recombination reaction, for example, reduced the apparent diffusivity in the vacuum desorption experiments. This hypothesis, suggested by Buxbaum et al. (1980) and Talbot (1981), is supported by the recombination rate experiments of Jung (1973-4) and also by the fact that the apparent diffusivity measured by Talbot et al. (1980) increased when hydrogen was added to the sweep gas.

Close agreement is found among experiments where no surface resistance was possible: Carlson et al. (1966), Fresius et al. (1972), and Fresius et al. (1976). Using a least squares fit for the data in these references, the diffusivity of protium in yttrium is calculated to be

$$\log_{10}(D \pm 20\%) = -2.425 - 2402/T. \quad (8)$$

This equation is represented by the solid line in Fig. 1.

IV. ISOTOPE EFFECTS IN YTTRIUM-HYDROGEN

At least two different approaches can be used to predict the isotope effect in yttrium-hydrogen diffusion. One approach is purely classical; as described by Zener (1950),

$$\begin{aligned} \frac{D_{H-Y}}{D_{T-Y}} &= \frac{\sqrt{M_1}}{\sqrt{M_3}} \\ &= \frac{1}{\sqrt{3}} \end{aligned} \quad (9)$$

where M_1 and M_3 are the atomic masses of protium and tritium respectively.

A compendium diffusion study by Volkyl and Alefield (1978) shows many striking departures from the square-root-of-mass dependence of Eq. (9). The most pronounced of these effects is seen at temperatures below 400°C, and for hydrogen isotopes in the following host metals: palladium, niobium, and vanadium. Eqs. (8) and (9) predict that the diffusivity of tritium in yttrium is

$$\log_{10} D (\pm 30\%) = -2.663 - 2402/T. \quad (10)$$

Another approach, described by Buxbaum (1981), predicts a diffusivity relation which should be applicable over a wider range of temperatures. The author assumes the entire isotope effect is due to differences in the zero-point-energy contribution to the activation energy for diffusion.

$$\frac{D_{H-Y}}{D_{T-Y}} = \exp \frac{-\beta(\Delta H_1 - \Delta H_3)}{R T_m} - \exp \frac{(\Delta H_1 - \Delta H_3)}{RT} \quad (11)$$

where T_m is the melting temperature of yttrium, 1768 K; ΔH_1 is the activation energy for protium diffusion in yttrium, 7.65×10^{-13} ergs/atom (10990 cal/g-atom); β is a dimensionless elastic constant, approximately equal to .35; and $(\Delta H_1 - \Delta H_3)$ is the zero-point energy difference for protium and tritium in yttrium. For a sinusoidal, one-dimensional potential,

$$\begin{aligned} (\Delta H_1 - \Delta H_3) &= \frac{h}{2\alpha} \sqrt{(\Delta H_1 + \Delta H_3)} \left(1/\sqrt{M_1} - 1/\sqrt{M_3} \right) \\ &= 4.95 \times 10^{-14} \text{ ergs/atom} \\ &= 710 \text{ cal/g-atom.} \end{aligned} \quad (12)$$

Here h is Planck's constant, 6.657×10^{-27} erg s; M_1 and M_3 are the atomic masses of protium and tritium, 1.66×10^{-24} and 4.98×10^{-24} g/atom respectively; and α is the distance between nearest-neighbor interstitial sites in yttrium, 297×10^{-8} cm.

From Eqs. (8), (11), and (12), the diffusivity of tritium in yttrium is predicted to be

$$D = (0.00406 \pm 0.0006) \exp [(11700 \pm 800)/RT]$$

$$\log_{10} D (\pm 20\%) = -2.391 - 2558/T. \quad (13)$$

One important application of Eq. (13) is in choosing the thickness for an absorber column using yttrium metal as a tritium getter. As an example calculation, consider an absorber which operates for 24 hours at 200°C before being regenerated. At this temperature

$$D_{Y-T} = 1.60 \times 10^{-8}.$$

The one-dimensional penetration depth η , cm, is given by

$$\eta = \sqrt{\pi D t} \quad (14)$$

where t is the sorption time, s. For the conditions specified above,

$$\begin{aligned} \eta &= \sqrt{(3.14) (1.60 \times 10^{-8}) (86400)} \\ &= 0.065 \text{ cm.} \end{aligned}$$

One may now size the metal thickness by setting it equal to some factor of the penetration depth, preferably one to two times η (Buxbaum, 1981). Sheet thicknesses, calculated in this manner, are well within the range available from commercial distributors.

V. ACKNOWLEDGMENT

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FIGURE CAPTIONS

Fig. 1 Diffusivity of Hydrogen in Yttrium.

Fig. 1