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Temperature-Dependent Ordinary and Thermal Diffusion of Hydrogen Isotopes through Thermonuclear Reactor Components

by

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TEMPERATURE-DEPENDENT ORDINARY AND THERMAL DIFFUSION OF HYDROGEN ISOTOPES THROUGH THERMONUCLEAR REACTOR COMPONENTS

by

John H. Pendergrass

ABSTRACT

To permit more accurate calculations of tritium permeation for design purposes, theoretical expressions for quasi-unidirectional ordinary diffusion of hydrogen isotopes through nonisothermal plane, cylindrical shell, and spherical shell barriers are presented. Arrhenium-type dependence of mass diffusivity on temperature and steady-state constant-thermal-conductivity temperature gradients through the barriers are considered.

Analyses that consider thermal diffusion with both constant and temperature-dependent heat of transport are also presented. Other topics discussed are amounts of dissolved hydrogen, variable-thermal-conductivity temperature profiles, hydrogen isotope trapping by chemical impurities, crystal lattice imperfections, and grain boundaries, and mixing rules for dilute dissolution of hydrogen isotope mixtures in metals.

Numerical results are given which reveal that neglect of thermal diffusion can lead to errors of up to several hundred percent in calculations of hydrogen isotope transfer through reactor components having large temperature gradients through them. Calculations of combined ordinary and thermal diffusion that rigorously treat the temperature dependences of thermo-physical properties typically yield results that differ by only a few percent from results based on physical property evaluations at the arithmetic average of barrier face temperatures.

I. INTRODUCTION

Accurate prediction of tritium migration within, and from, thermonuclear reactor power systems is necessary to the design function for several reasons. First, and most crucial, is protection of the citizenry and the environment from potential radioactivity hazards associated with tritium. Second, tritium is rare in nature and can presently be manufactured in quantity only through relatively inefficient processes in fission reactors; until it can be bred on

a large scale in lithium-containing blankets of thermonuclear reactors, it will be extremely expensive and must be used as efficiently as possible. In fact, some proposed thermonuclear reactor designs may not permit intrinsic breeding ratios greatly in excess of unity and may thus consume themselves all the tritium they breed; and even for designs with relatively high tritium breeding ratios, good recovery under difficult circumstances will be necessary, and virtually complete recovery may be desirable, if nonbreeding reactors are to be supported to the desired extent.

Preliminary assessments of laser fusion reactor systems operation indicate that to accomplish the objectives listed above, tritium concentrations throughout thermonuclear reactors must be maintained at very low levels (perhaps in the parts-per-million range or less), tritium leakage rates from thermonuclear reactors must be maintained at very low levels (a few curies per day or less seems likely), and efficient processes for tritium separation and recovery capable of operating with such low tritium concentrations must be provided through appropriate engineering design. The low concentrations which must be maintained and the low leakage rates which must be assured present formidable technological problems, to which only extensive research and development programs will provide solutions.

Thin, hot reactor components lying directly across pathways leading to reactor surroundings, e.g., steam-cycle heat-exchanger tubes, are most critical with respect to tritium escape from the system. High temperatures mean high diffusivities for hydrogen isotopes, and thin barriers mean lower resistances to their diffusion. Besides, hydrogen isotope diffusivities in metals are relatively high, often exceeding those of heavier interstitials such as oxygen and nitrogen by factors of the order of fifteen to twenty orders of magnitude at room temperature.

The effects of variations in thermophysical properties due to temperature variations through nonisothermal reactor components on tritium transfer through the components do not appear to have been addressed in earlier investigations of tritium migration in thermonuclear reactor systems.^{1,2} The consequences of neglect of the effects on thermophysical properties of strong temperature variation through metal barriers of important geometries, e.g., (1) plane, (2) cylindrical shell, and (3) spherical shell geometries, on the transport of hydrogen isotopes through the barriers due to ordinary diffusion will be examined in detail and appropriate design equations will be developed. The effects of

temperature variations along such barriers on the transfer of hydrogen isotopes through them have been factored into analyses of tritium migration in thermonuclear reactor systems in the past^{1,2} and will not be treated, because temperature gradients and hydrogen isotope concentration gradients along such barriers are considered sufficiently small to allow the use of quasi-unidirectional approximations for most design purposes.

If temperature gradients through thermonuclear reactor components are large, the flux of tritium through such components due to thermal diffusion can approach or surpass that due to ordinary diffusion. Thermal diffusion of hydrogen isotopes has apparently not been treated in previous analyses of tritium migration in proposed thermonuclear reactor systems, and also merits examination in detail. Temperature variation of thermophysical properties and important geometries, such as the three geometries mentioned in the preceding paragraph, will be treated.

We will confine our presentation to steady-state isotope transfer, because it is deemed more important for design purposes than the considerably more difficult analyses of unsteady-state transfer through thin, hot reactor components.

Some phenomena, such as the trapping by chemical impurities, lattice imperfections, or grain boundaries of hydrogen isotope atoms diffusing through metals--and their effect on transport and solubility, and mixing rules for the dissolution of hydrogen isotope mixtures in metals, which might lead to the invalidation of the theory developed herein--are also deserving of attention. The approximations, postulates, and assumptions leading to Sieverts' Law for the solubility of hydrogen isotopes in metals are important to an understanding of proposed hydrogen isotope mixing rules. These topics do not appear to have received adequate attention in connection with tritium migration in thermonuclear reactor systems.

Other important questions that will be addressed in subsequent reports include isotopic influences on diffusivities and solubilities, the effect of variations in carrier-metal composition and crystal structure on diffusivities and solubilities, the effects of corrosion and oxidation layers on metal surfaces, on rates of permeation of hydrogen isotopes through metal barriers, and the resistance to the transfer of hydrogen isotopes through phases external to metal barriers.

II. REVIEW OF ISOTHERMAL CASE

If we assume that (1) Fick's law of diffusion is valid for the entire range of dissolved hydrogen isotope concentrations of interest, (2) simultaneously diffusing hydrogen isotope atoms do not interact, (3) concentrations do not vary along the barrier, and (4) the barrier is isothermal, the following respective expressions for the steady-state flux J of a hydrogen isotope through a plane barrier of uniform thickness, a cylindrical shell, and a spherical shell are readily derived. For a plane barrier, the flux is given by

$$J = \frac{D_o e^{-\frac{Q_D}{RT}}}{(x_2 - x_1)} (C_1 - C_2) , \quad (1)$$

for a cylindrical shell by

$$J_{\theta L} = \frac{D_o e^{-\frac{Q_D}{RT}}}{\ln(r_2/r_1)} (C_1 - C_2) , \quad (2)$$

and for a spherical shell by

$$J_{\Omega} = \frac{r_1 r_2 D_o e^{-\frac{Q_D}{RT}}}{(r_2 - r_1)} (C_1 - C_2) . \quad (3)$$

The temperature dependence of the diffusion coefficient has been represented in terms of an Arrhenius-type expression, which appears to be adequate for the representation of temperature dependences of available experimental diffusivity data. The three geometries considered and part of the associated notation are illustrated in Fig. 1. Note, particularly, that the concentrations C_1 and C_2 are those in the bulk metal just below the surfaces. If resistances to transfer through the surfaces or in the phases external to the metal barriers are significant, then C_1 and C_2 will not correspond to the concentrations just outside the metal surfaces or in the bulk external phases. Note also that J , $J_{\theta L}$, and J_{Ω} are defined differently and do not have the same dimensions. However, the validity of the preceding results do not depend upon the validity of any particular law of solubility, e.g., Sieverts' Law, for hydrogen isotopes in metals.

Fig. 1.

(a) Plane barrier, (b) cylindrical shell barrier, (c) spherical shell barrier.

Other tacit assumptions are involved and will be discussed in following paragraphs.

No published information seems to cast doubt upon the validity of the first postulate for systems of interest in thermonuclear power generation when temperatures and hydrogen isotope partial pressures are sufficiently high, provided the partial pressure is not so high that it causes formation of a second, i.e., hydride phase. However, at sufficiently low hydrogen isotope concentrations, chemical interactions with small amounts of impurities contained in host metals, e.g., oxygen, or sulfur, could result in apparent deviations from Fick's law under transient conditions. Such deviations might not be noticed at higher concentrations of the diffusing isotopes because only insignificant quantities of the diffusing isotopes are involved in the chemical reactions when impurity concentrations are small. This mechanism has been suggested, e.g., by McNabb and Foster³ as an explanation for apparent deviations from Fick's law for transient diffusion of hydrogen through iron and various steels at temperatures below a few hundred degrees centigrade. The experimental data of McNabb and Foster indicate that such chemical combinations of hydrogen with impurities are unstable at higher temperatures. This phenomenon is discussed in more detail in a subsequent section.

The second postulate, which has received virtually no attention but does not appear unreasonable for low hydrogen isotope concentrations, states that at

low concentrations most interactions of hydrogen isotope atoms will be with host metal atoms rather than with other hydrogen isotope atoms.

The third postulate may be relaxed somewhat if the variation in isotope concentration along the barrier is modest, i.e., when the variations in concentration through the barrier are affected significantly only by variations in boundary conditions, e.g., the concentrations at the barrier faces, and when transport within the barrier parallel to the barrier faces is negligible. This is the quasi-one-dimensional case. Changes in hydrogen isotope concentration along the barrier faces can be deduced from isotope conservation principles applied to the phases external to the barrier. Concentration gradients along barriers are expected to be modest because of low fluxes through barriers at the low tritium concentrations that apparently must be maintained in thermonuclear reactors to limit tritium losses to the environment to the rates considered necessary for safety and economic reasons. Temperature gradients along the barriers may be larger, e.g., along heat exchanger tubes, and each case should be examined for applicability of the quasi-unidimensional approximation with respect to temperature distributions. However, significant inaccuracies are not expected to arise often if this quasi-unidirectional approximation is applied with respect to temperature variation.

Also implicit in Eqs. (1), (2), and (3) is the assumption that mass diffusivity of a hydrogen isotope in a metal is not a function of direction, at least not for the cylindrical and spherical cases. For single-crystal barriers this statement is equivalent to the assumption of a cubic crystalline lattice. For polycrystalline barriers--the practical case--random orientation of individual crystals ensures that mean diffusivity is independent of direction. The mass diffusivity has also been tacitly assumed to be independent of concentration, which should be a very good approximation for dilute solutions.

A reasonable amount of experimental evidence indicates that diffusion along grain boundaries does not represent a significant contribution to the diffusive flux of hydrogen isotopes in polycrystalline materials. For example, measurements of Edwards⁴ of protium permeation through single-crystal barriers of iron and through polycrystalline barriers of the same dimensions, obtained by recrystallizing the single-crystal barriers, revealed negligible differences in permeation rates under identical experimental conditions. Smithells and Ransley⁵ compared protium permeation rates through two different sections of the same iron tube, one fine-grained and one single-crystal, and arrived at the same con-

conclusion. Ogurtani⁶ also reported no significant effect of grain size on diffusivity for protium in niobium.

Note, however, that this conclusion is based upon experiments conducted at relatively high concentrations, and that similar experiments at sufficiently low concentrations might reveal that this conclusion needs modification for sufficiently low concentrations. For example, Elleman and Verghese⁷ have obtained limited evidence for low-concentration recoil implantation of tritium from neutron-induced transformation of a surface layer of ${}^6\text{Li}_2\text{CO}_3$ on 304-stainless steel, which suggests that for this system, grain-boundary diffusion overshadows bulk metal diffusion. However, similar behavior was not observed in analogous experiments with niobium. Furthermore, the experiments were nonsteady state, which could mean that grain-boundary physicochemistry may have influenced the transport in a manner not consistent with steady-state transport.

Further restrictions--i.e., that (1) the only significant resistance to hydrogen isotope permeation through the barrier is offered by the bulk metal, (2) the solubility of a particular hydrogen isotope is not affected by the presence of other hydrogen isotopes, and (3) Sieverts' law of solubility applies at hydrogen isotope concentrations of interest--allow the permeation fluxes to be expressed in terms of hydrogen isotope partial pressures in equilibrium with the dissolved hydrogen isotope concentrations. Thus, the following expressions apply for the plane barrier, the cylindrical shell, and the spherical shell, respectively:

$$J = \frac{D_o e^{-\frac{Q_D}{RT}}}{(x_2 - x_1)} K_S^o e^{-\frac{Q_S}{RT}} (p_1^{1/2} - p_2^{1/2}) = \frac{P_o e^{-\frac{Q_P}{RT}}}{(x_2 - x_1)} (p_1^{1/2} - p_2^{1/2}) ; \quad (4)$$

$$J_{OL} = \frac{D_o e^{-\frac{Q_D}{RT}}}{\ln(r_2/r_1)} K_S^o e^{-\frac{Q_S}{RT}} (p_1^{1/2} - p_2^{1/2}) = \frac{P_o e^{-\frac{Q_P}{RT}}}{\ln(r_2/r_1)} (p_1^{1/2} - p_2^{1/2}) , \quad (5)$$

and:

$$J_{\Omega} = \frac{r_1 r_2 D_o e^{-\frac{Q_D}{RT}}}{(r_2 - r_1)} K_S^o e^{-\frac{Q_S}{RT}} (p_1^{1/2} - p_2^{1/2}) = \frac{r_1 r_2 P_o e^{-\frac{Q_P}{RT}}}{(r_2 - r_1)} (p_1^{1/2} - p_2^{1/2}) , \quad (6)$$

using Sieverts' law of solubility

$$C = K_S p^{1/2} = K_S^o e^{-\frac{Q_S}{RT}} p^{1/2}, \quad (7)$$

where

$$p = p_o e^{-\frac{Q_p}{RT}} = (p_o K_S^o) e^{-\frac{(Q_D + Q_S)}{RT}}. \quad (8)$$

The concentration in Sieverts' law is usually expressed as an atom ratio, which approaches the atom fraction as dissolved hydrogen isotope concentration approaches zero. The concentration in g-atom/cm³ may be expressed in terms of the atom ratio according to

$$C = \frac{N \rho_m}{M_m}. \quad (9)$$

Use of the most common form of Sieverts' law therefore requires multiplying the left-hand members of Eqs. (4), (5), and (6) by (ρ_m/M_m) . The density and molecular weight of the pure metal have been used, and the difference between atom fraction and atom ratio has been ignored, because current interest is focused on dilute solutions of hydrogen isotopes in metals. It must also be remembered that at low hydrogen isotope partial pressures, dissociation of the diatomic molecules occurs to a significant extent and this must be taken into consideration.

The first of these additional postulates is not valid for sufficiently low dissolved-hydrogen isotope concentrations. Permeation through a metal barrier typically involves several transfer steps, i.e., transport to the inside barrier surface, adsorption onto the inside barrier surface, dissolution of the adsorbed molecules in the bulk metal as atoms, diffusion through the bulk-metal atoms, coming out of solution and recombining to form molecules, desorption of adsorbed molecules from the outside barrier surface, and transport from the outside barrier surface when the metal surfaces are clean. If corrosion layers are present on the barrier surfaces, further resistances to transfer are involved. It can be shown--see, e.g., Ash and Barrer⁸ and Levin and Stickney⁹--that the resistance to transfer, due to the bulk metal, can become comparable to other resistances or even negligible if the hydrogen isotope partial pressure becomes very small.

The second postulate has received only minimal consideration. However, it deserves greater attention because significant amounts of protium and deuterium formed or introduced into reactor systems, e.g., through (n,p) reactions of thermonuclear neutrons with structural materials and from unburnt fuel respectively, will be associated with tritium in thermonuclear reactors. Previously published analyses have generally ignored these nonradioactive hydrogen isotopes and their possible effects on tritium migration. Hydrogen embrittlement by all three isotopes may also present problems and may require accurate analysis of migration for all three isotopes. This question is addressed in detail in a subsequent section.

Although there has been much controversy and conflicting evidence concerning the validity of Sieverts' law of solubility of hydrogen isotopes in metals for very low partial pressures, the majority of recent careful work appears to confirm the validity of this law for many sufficiently pure metals of sufficiently low surface-to-volume ratios down to partial pressure approaching those of practical concern in thermonuclear reactors. Other recent studies suggest that modest deviations from Sieverts' law may be expected for sufficiently low pressures and certain metals, but that Sieverts' law still represents a useful first-order approximation. The deviations from Sieverts' law apparently generally become less severe as temperatures increase. Examples of recent studies addressed to this question include those of Ricca and Giorgi,¹⁰ Giorgi and Ricca,¹¹ Ricca,^{12,13} Mallet and Albrecht,¹⁴ and McQuillan and Wallbank.^{15,16}

III. ANALYSIS, TAKING INTO CONSIDERATION TEMPERATURE DEPENDENCE OF DIFFUSIVITY, BUT NOT THERMAL DIFFUSION

As noted earlier, no attempt has been made in analyses of tritium migration in thermonuclear reactor systems published to date, e.g., by Maroni¹ and Stickney,² to include the effects of temperature variation through metal barriers on the diffusion of hydrogen isotopes through these barriers. Table I illustrates that significant effects due to the typically strong variation of the diffusion coefficient with variations in temperature through metal barriers can arise under typical thermonuclear reactor operating conditions.

Because thermophysical property data for evaluation of theoretical diffusion expressions are sometimes limited, the effects of nonisothermality will be included in our analyses in a stepwise manner to provide solutions involving increasing levels of sophistication corresponding to the increasing availability of thermophysical property data.

TABLE I

EFFECT OF VARIATION OF TEMPERATURE ACROSS A METAL BARRIER ON THE HYDROGEN ISOTOPE DIFFUSIVITY OR PERMEABILITY THROUGH THAT BARRIER WHEN DIFFUSIVITY OR PERMEABILITY IS REPRESENTED IN TERMS OF AN ARRHENIUS EXPRESSION

Temperature Level (Higher), K	Temperature Drop Across Barrier, K	Activation Energy for Permeability or Diffusivity, g-cal/g-at.	Ratio of Permeability or Diffusivity at Higher Temperature to that at Lower Temperature
1 000	10 ^a	5 000 ^c	1.025
	100 ^b		1.323
500	10	5 000	1.108
	100		3.519
1 000	10	10 000 ^c	1.052
	100		1.749
500	10	10 000	1.228
	100		12.238
1 000	10	20 000 ^c	1.107
	100		3.059
500	10	20 000	1.508
	100		153.348

a - Low for a heat exchanger.

b - Typical of a heat exchanger.

c - Typical of a range of experimental values (examples: hydrogen in niobium, 5 200 g-cal/g-at.; hydrogen in 304-stainless steel, 16 100 g-cal/g-at.; hydrogen in aluminum, 30 832 g-cal/g-at.; Maronil).

The complications associated with the representations of hydrogen isotope fluxes in terms of partial pressures, corresponding to the second set of postulates, will be avoided by expressing the fluxes in terms of dissolved isotope concentrations. In any event, under conditions for which the resistance to transfer of the bulk metal is comparable to the other resistances to transfer, the resistance of the bulk metal is most logically expressed in terms of dissolved-isotope concentrations. All the formulae derived for J , $J_{\theta L}$, and J_{Ω} in subsequent sections may be readily combined with Sieverts' law if expressions are to be obtained for these quantities in terms of partial pressures. The resulting formulae will be useful whenever resistances to transfer other than bulk-metal resistances are negligible.

Temperature gradients through barriers will be taken as quasi-one-dimensional, i.e., variations in temperature through the barrier will be assumed to be much greater than variations along the barrier so that the local temperature variation through the barrier is affected significantly by variations along the barrier only through an effect on the boundary conditions, i.e., by the surface temperatures. Thermal-energy transport parallel to the barrier surfaces will be neglected. Temperature variations along the barrier surface can be computed through application of energy conservation principles to the phases exterior to the barrier. This approach has been almost universally adopted in heat-exchanger analysis and design.

The variation in temperature through the barrier will be expressed in terms of an appropriate average thermal conductivity. Although thermal conductivities are functions of temperature, their variations with temperature are generally quite modest in comparison with the temperature dependences of mass diffusivities. Methods for obtaining solutions for the cases in which the thermal conductivity is represented as a linear or polynomial function of temperature are sketched in Appendix A.

Based on these approximations, the temperature distributions in a plane barrier, a pipe wall, and a spherical shell, are readily deduced. They are respectively:

$$T = \frac{(T_1 - T_2)}{(x_2 - x_1)} (x_1 - x) + T_1 ; \quad (10)$$

$$T = \frac{(T_1 - T_2)}{\ln(r_2/r_1)} \ln(r_1/r) + T_1 ; \quad (11)$$

and

$$T = \frac{r_1 r_2 (T_1 - T_2)}{(r_2 - r_1)} \frac{(r_1 - r)}{r r_1} + T_1 . \quad (12)$$

Under conditions of steady-state operation, the amount of tritium dissolved in thin, hot barriers--small compared to the total tritium inventory of a thermonuclear reactor system--will be of limited interest. Furthermore, evaluation of theoretical formulae for absorbed amounts will be difficult. Therefore, only a limited discussion of this aspect of tritium distribution in thermonuclear reactor systems is presented in Appendix B.

Plane Barrier

In terms of Cartesian coordinates, the unidirectional diffusion flux is given by Fick's law

$$J = - D \frac{dC}{dx} = - D_0 e^{-\frac{Q_D}{RT}} \frac{dC}{dx} \quad (13)$$

and is a constant under steady-state conditions. An appropriate auxiliary condition is

$$C = C_1, T = T_1, @ x = x_1 . \quad (14)$$

It is convenient to substitute for x in Eq. (13) using Eq. (10) for the temperature distribution

$$\frac{dT}{dx} = - \frac{(T_1 - T_2)}{(x_2 - x_1)}, \quad \frac{dC}{dx} = \frac{dC}{dT} \frac{dT}{dx} \quad (15)$$

to obtain

$$J = D_0 \frac{(T_1 - T_2)}{(x_2 - x_1)} e^{-\frac{Q_D}{RT}} \frac{dC}{dT} . \quad (16)$$

The further substitution

$$T = \frac{1}{\tau}, \quad dT = - \frac{1}{\tau^2} d\tau \quad (17)$$

is also convenient. In terms of τ , Eq. (15) becomes

$$J = - \mathbb{D}_0 \frac{(T_1 - T_2)}{(x_2 - x_1)} \frac{e^{-\frac{Q_D}{R} \tau}}{\tau^2} \frac{dC}{d\tau}, \quad (18)$$

with the auxiliary condition, Eq. (14), becoming

$$C = C_1 @ \tau = \tau_1. \quad (19)$$

The solution, obtained through integration by parts, to Eqs. (18) and (19) is

$$C = C_1 + \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \left(\frac{e^{-\frac{Q_D}{R} \tau}}{\tau} - \frac{e^{-\frac{Q_D}{R} \tau_1}}{\tau_1} \right) - \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \frac{Q_D}{R} \int_{\tau_1}^{\tau} \frac{e^{-\frac{Q_D}{R} \tau}}{\tau} d\tau. \quad (20)$$

The definite integral may be expressed in terms of the standard integral

$$E_1(z) = \int_z^{\infty} \frac{e^{-u}}{u} du \quad (21)$$

to obtain

$$\begin{aligned} C &= C_1 + \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \left(\frac{e^{-\frac{Q_D}{R} \tau}}{\tau} - \frac{e^{-\frac{Q_D}{R} \tau_1}}{\tau_1} \right) \\ &+ \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \frac{Q_D}{R} \left[E_1\left(-\frac{Q_D}{R} \tau\right) - E_1\left(-\frac{Q_D}{R} \tau_1\right) \right] \\ &= C_1 = \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \left[\zeta\left(\frac{Q_D}{R} \tau\right) + \frac{Q_D}{R} \eta\left(\frac{Q_D}{R} \tau\right) \right] \end{aligned} \quad (22)$$

where

$$\zeta(\lambda\tau) = \frac{e^{\lambda\tau}}{\tau} - \frac{e^{\lambda\tau_1}}{\tau_1},$$

$$\eta(\lambda\tau) = E_1(-\lambda\tau) - E_1(-\lambda\tau_1) . \quad (23)$$

Efficient approximate formulae for computation of $E_1(x)$ are discussed in Appendix C. The only other recourse for computation of numerical values for $E_1(x)$ appears to be the evaluation of an infinite series that converges slowly for large values of x , and large values of $[(Q_D/R)\tau_1]$ are common in practical cases, or numerical quadrature.

The quantity of greatest interest is generally the flux, rather than the concentration profile. The flux is most easily computed by substituting the (presumably) known condition at the other barrier face

$$C = C_2 \text{ @ } \tau = \tau_2 , \quad (24)$$

and solving for the flux to obtain

$$J = D_0 \frac{(T_1 - T_2)}{(x_2 - x_1)} F_1 (C_1 - C_2) , \quad (25)$$

where

$$F_1 = - \frac{1}{\left\{ \left(\frac{Q_D}{R} \tau_2 \right) + \frac{Q_D}{R} \eta \left(\frac{Q_D}{R} \tau_2 \right) \right\}} . \quad (26)$$

The resistance to transfer of the bulk metal, defined by

$$J = \frac{1}{R} (C_1 - C_2) , \quad (27)$$

is given by

$$R = \frac{(x_2 - x_1)}{D_0 (T_2 - T_1) F_1} . \quad (28)$$

The total rate of transfer through the barrier is given by

$$J = \int_A J da . \quad (29)$$

Cylindrical Shell

Pick's law for a cylindrical shell may be expressed in the form

$$J = - D_0 e^{-\frac{Q_D}{RT}} \frac{dC}{dr}, \quad (30)$$

but J is not a constant function of r in this case. However,

$$J_{\theta L} = rJ = - D_0 e^{-\frac{Q_D}{RT}} r \frac{dC}{dr} \quad (31)$$

is a constant function of r . With barrier-face conditions

$$C = C_1 \text{ @ } \tau = \tau_1, \quad C = C_2 \text{ @ } \tau = \tau_2, \quad (32)$$

substitution of temperature distribution, Eq. (11), and change of variables corresponding to those for the plane wall, one can show that for the cylindrical shell case

$$C = C_1 + \frac{\ln(r_2/r_1)}{(T_1 - T_2)} \frac{J_{\theta L}}{D_0} \left[\zeta\left(\frac{Q_D}{R} \tau\right) + \frac{Q_D}{R} \eta\left(\frac{Q_D}{R} \tau\right) \right] \quad (33)$$

and

$$J_{\theta L} = D_0 \frac{(T_1 - T_2)}{\ln(r_2/r_1)} F_1(C_1 - C_2) \quad (34)$$

$$R_{\theta L} = \frac{\ln(r_2/r_1)}{D_0(T_1 - T_2)F_1} \quad (35)$$

$$J = \theta \int_0^L J \, d\ell. \quad (36)$$

Spherical Shell

in similar fashion, for a spherical shell

$$J_{\Omega} = r^2 J = - D_0 e^{-\frac{Q_D}{RT}} r^2 \frac{dC}{dr} \quad (37)$$

is a constant function of r and corresponding solutions are

$$C = C_1 + \frac{(r_2 - r_1)}{(T_1 - T_2)r_1 r_2} \frac{J_{\Omega}}{D_0} \left[\zeta\left(\frac{Q_D}{R} \tau\right) + \frac{Q_D}{R} \eta\left(\frac{Q_D}{R} \tau\right) \right] \quad (38)$$

$$J_{\Omega} = D_0 \frac{(T_1 - T_2)r_1r_2}{(r_2 - r_1)} F_1(C_1 - C_2) \quad (39)$$

$$R_{\Omega} = \frac{(r_2 - r_1)}{D_0(r_1r_2)F_1} \quad (40)$$

and

$$J = \int_{\Omega} J d\omega. \quad (41)$$

IV. STEADY-STATE ANALYSIS WITH BOTH TEMPERATURE DEPENDENCE OF ORDINARY DIFFUSIVITY AND THERMAL DIFFUSION TAKEN INTO CONSIDERATION

As Table II illustrates, the flux of hydrogen isotopes due to thermal diffusion can greatly exceed that due to ordinary diffusion under typical thermonuclear reactor operating conditions. No published prior analyses of tritium migration in thermonuclear reactor systems seems to exist which considers the effects of thermal diffusion. The analyses concerned with combined ordinary and thermal diffusion transport of hydrogen isotopes through metal barriers, which follow, will be based upon the same assumptions and approximations upon which the preceding analyses not treating thermal diffusion are based. In particular, the same three geometries are investigated, the quasi-unidirectional transfer approximation is employed, and the same temperature distributions are postulated.

The flux of a substance in dilute solution in a stationary solvent in combined ordinary and thermal diffusion may be expressed as

$$\vec{J} = - \frac{DC}{RT} \left[RT \left\{ 1 + \frac{\partial[\ln(\gamma)]}{\partial[\ln(C)]} \right\} \nabla[\ln(C)] + \frac{Q^*}{T} \nabla T \right] \quad (42)$$

e.g., according to Howard and Lidiard.¹⁷ For a sufficiently dilute solution

$$\frac{\partial[\ln(\gamma)]}{\partial[\ln(C)]} \approx 0, \quad (43)$$

and Eq. (42) reduces to

$$\vec{J} = - D \left[\nabla(C) + \left(\frac{Q^*}{RT^2} \nabla T \right) C \right] \quad (44)$$

for dilute solutions.

TABLE II

COMPARISON OF HYDROGEN-ISOTOPE FLUXES THROUGH METAL BARRIERS DUE TO ORDINARY DIFFUSION AND TO THERMAL DIFFUSION WHEN THE PRINCIPAL RESISTANCE TO TRANSFER IS THE BULK METAL

$d[\ln(N)]/dx$, Logarithmic Concentration Gradient in Metal Barrier, cm^{-1}	dT/dx , Temperature Gradient in Metal Barrier, K/cm	Effective Mean Tem- perature, K	$1Q^*1$ Absolute Value of Heat of Transport, g-cal/g-at.	$RT \frac{d[\ln(N)]}{dx} / \frac{1Q^*1}{T} \frac{dT}{dx}$, Absolute Value of Ratio of Ordinary Diffusion Flux to Thermal Diffusion Flux
-6.908 ^a	- 10 ^d	1 000	1 000g 5 000g 10 000g	1373. 275. 137.
-6.908	-100 ^e	1 000	1 000 5 000 10 000	137. 27.5 13.7
-6.908	-500 ^f	1 000	1 000 5 000 10 000	27.5 5.49 2.75
-4.605 ^b	- 10	1 000	1 000 5 000 10 000	915. 183. 91.5
-4.605	-100	1 000	1 000 5 000 10 000	91.5 18.3 9.15
-4.605	-500	1 000	1 000 5 000 10 000	18.3 3.66 1.83
-2.303 ^c	- 10	1 000	1 000 5 000 10 000	457. 91.5 45.7
-2.303	-100	1 000	1 000 5 000 10 000	45.7 9.15 4.57
-2.303	-500	1 000	1 000 5 000 10 000	9.15 1.83 0.915
-6.908	- 10	500	1 000 5 000 10 000	343. 68.6 34.3
-6.908	-100	500	1 000 5 000 10 000	34.3 6.86 3.43
-6.908	-500	500	1 000 5 000 10 000	6.87 1.37 0.686
-4.605	- 10	500	1 000 5 000 10 000	229. 45.8 22.9

TABLE II (Continued)

$d[\ln(N)]/dx$, Logarithmic Concentration Gradient in Metal Barrier, cm^{-1}	dT/dx , Temperature Gradient in Metal Barrier, K/cm	Effective Mean Tem- perature, K	$ Q^* $ Absolute Value of Heat of Transport, g-cal/g-at.	$RT \frac{d[\ln(N)]}{dx} / \frac{ Q^* }{T} \frac{dT}{dx}$, Absolute Value of Ratio of Ordinary Diffusion Flux to Thermal Diffusion Flux
-4.605	-100	500	1 000	22.8
			5 000	4.58
			10 000	2.29
-4.605	-500	500	1 000	4.58
			5 000	0.915
			10 000	0.457
-2.303	- 10	500	1 000	114.
			5 000	22.9
			10 000	11.4
-2.303	-100	500	1 000	11.4
			5 000	2.29
			10 000	1.14
-2.303	-500	500	1 000	2.28
			5 000	0.457
			10 000	0.228

a - Corresponds to a drop in concentration across the barrier by a factor of the order of 1 000.

b - Corresponds to a drop in concentration across the barrier by a factor of the order of 100.

c - Corresponds to a drop in concentration across the barrier by a factor of the order of 10.

d - Low for a heat exchanger.

e - Typical for heat exchangers.

f - Typical for a bare hot pipe.

g - Representative of the range of available measured values (examples: hydrogen in iron, 683 K, -8100 g-cal/g-at.; deuterium in nickel, 993 K, -800 g-cal/g-atm.; Gonzales and Orianil¹⁸; deuterium in zircaloy-2, 635 K, 6800 g-cal/g-atm.; Sawatzky¹⁹).

Frequently the only available experimental data for the heat of transport for a particular system consist of a single value at one temperature. Therefore, an analysis will be presented for the case in which the heat of transport is a constant. The limited experimental evidence for thermal diffusion of gases in solids, e.g., presented by Gonzales and Oriani¹⁸ for protium and deuterium in iron and nickel, suggests, however, that significant variations in the value of the heat of transport with variation in temperature typically do occur. Available data, Fig. 2, also suggest that the dependence of the heat of transport on temperature may be accurately approximated as linear over wide temperature ranges. Therefore, this case will also be analyzed. Note that the heat of transport can be either positive or negative in a given temperature range, depending on the host metal. If negative, the effect of thermal diffusion will be to oppose ordinary diffusion and to reduce the net transfer rate if temperature and concentration gradients have the same signs. If positive, the total rate of transfer will be greater than the rate due to ordinary diffusion alone. However, the temperature coefficient of the heat of transport for hydrogen isotopes in metals appears to be positive for all host metals, e.g., according to Gonzales and Oriani.¹⁸ Therefore, for sufficiently

Fig. 2
Temperature dependence of heat of transport (Gonzales and Oriani¹⁸): o is H in α -Fe; $\square$ is D in α -Fe; Δ is H in α -Ni; $\diamond$ is D in α -Ni; ∇ is H in γ -Fe_{0.6}Ni_{0.4}.

high temperatures the heat of transport will be positive if the linear dependence on temperature extends over a sufficiently wide temperature range. Stronger dependences of the heat of transport on temperature are considered briefly in Appendix D.

Constant Heat of Transport

Plane barrier. In terms of Cartesian coordinates, the unidirectional mass flux due to combined ordinary and thermal diffusion is given by

$$J = - D_0 e^{-\frac{Q_D}{RT}} \left(\frac{dC}{dx} + \frac{Q^*}{RT^2} \frac{dT}{dx} C \right). \quad (45)$$

The conditions at the barrier faces are the same as previously used for the plane barrier, the same temperature distribution is substituted, and the same change of variable is convenient. Corresponding solutions are

$$e^{-\frac{Q^*}{R} \tau} C = e^{-\frac{Q^*}{R} \tau_1} C_1 + \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{D_0} \left\{ \left[\frac{(Q_D - Q^*)}{R} \tau \right] + \frac{(Q_D - Q^*)}{R} \eta \left[\frac{(Q_D - Q^*)}{R} \tau \right] \right\}, \quad (46)$$

$$J = D_0 \frac{(T_1 - T_2)}{(x_2 - x_1)} F_2 (C_1 - C_2), \quad (47)$$

$$F_2 = - \frac{\left(e^{-\frac{Q^*}{R} \tau_1} C_1 - e^{-\frac{Q^*}{R} \tau_2} C_2 \right)}{[C_1 - C_2] \left\{ \left[\frac{(Q_D - Q^*)}{R} \tau_2 \right] + \frac{(Q_D - Q^*)}{R} \eta \left[\frac{(Q_D - Q^*)}{R} \tau_2 \right] \right\}}, \quad (48)$$

$$R = \frac{(x_1 - x_2)}{D_0 (T_1 - T_2) F_2}, \quad (49)$$

and

$$J = \int_A J da. \quad (50)$$

Cylindrical shell. Similarly, for the cylindrical shell barrier

$$J_{\theta L} = rJ = - D_0 e^{-\frac{Q_D}{RT}} r \left(\frac{dC}{dr} + \frac{Q^*}{RT^2} \frac{dT}{dr} C \right) = \text{constant} , \quad (51)$$

$$e^{-\frac{Q^*}{R} \tau} C = e^{-\frac{Q^*}{R} \tau_1} C_1 + \frac{\ln(r_2/r_1)}{(T_1 - T_2)} \frac{J_{\theta L}}{D_0} \left\{ \left[\frac{(Q_D - Q^*)}{R} \tau \right] + \frac{(Q_D - Q^*)}{R} \eta \left[\frac{(Q_D - Q^*)}{R} \tau \right] \right\} \quad (52)$$

$$J_{\theta L} = D_0 \frac{(T_1 - T_2)}{\ln(r_2/r_1)} F_2 (C_1 - C_2) , \quad (53)$$

$$R_{\theta L} = \frac{\ln(r_2/r_1)}{D_0 (T_1 - T_2) F_2} , \quad (54)$$

and

$$J = \theta \int_0^L J_{\theta L} d\ell . \quad (55)$$

Spherical shell. The corresponding differential and integral expressions for a spherical shell barrier are

$$J_{\Omega} = r^2 J = - D_0 e^{-\frac{Q_D}{RT}} r^2 \left(\frac{dC}{dr} + \frac{Q^*}{RT^2} \frac{dT}{dx} C \right) = \text{constant} , \quad (56)$$

$$e^{-\frac{Q^*}{R} \tau} C = e^{-\frac{Q^*}{R} \tau_1} C_1 + \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \frac{J_{\Omega}}{D_0} \left\{ \left[\frac{(Q_D - Q^*)}{R} \tau \right] + \frac{(Q_D - Q^*)}{R} \eta \left[\frac{(Q_D - Q^*)}{R} \tau \right] \right\} \quad (57)$$

$$J_{\Omega} = D_0 \frac{(T_1 - T_2) r_1 r_2}{(r_2 - r_1)} F_2 (C_1 - C_2) , \quad (58)$$

$$R_r = \frac{(r_2 - r_1)}{D_0 (T_1 - T_2) r_1 r_2 F_2} , \quad (59)$$

and

$$J = \int_{\Omega} J_{\Omega} dw . \quad (60)$$

Variable Heat of Transport

As noted previously, linear dependence of the heat of transport on temperature will also be treated, i.e., the case

$$Q^* = \alpha + \beta T \quad (61)$$

will be analyzed.

Plane barrier. The applicable equations and solutions are

$$J = - D_0 e^{-\frac{Q_D}{RT}} \left[\frac{dC}{dx} + \left(\frac{\alpha}{RT^2} + \frac{\beta}{RT} \right) \frac{dT}{dx} C \right] = \text{constant}, \quad (62)$$

$$\begin{aligned} \frac{e^{-\frac{\alpha}{R}\tau}}{\tau^{\frac{\beta}{R}}} C &= \frac{e^{-\frac{\alpha}{R}\tau_1}}{\tau_1^{\frac{\beta}{R}}} C_1 - \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{D_0} \int_{\tau_1}^{\tau} \frac{e^{\frac{(Q_D - \alpha)}{R}\tau}}{\tau^{\frac{\beta}{R} + 2}} d\tau \\ &= \frac{e^{-\frac{\alpha}{R}\tau_1}}{\tau_1^{\frac{\beta}{R}}} C_1 - \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{D_0} \sum_{n=0}^{\infty} \frac{\left(\frac{Q_D - \alpha}{R} \right)^n \left(\tau^{n - \frac{\beta}{R} - 1} - \tau_1^{n - \frac{\beta}{R} - 1} \right)}{n! (n - \frac{\beta}{R} - 1)} \\ &= \frac{e^{-\frac{\alpha}{R}\tau_1}}{\tau_1^{\frac{\beta}{R}}} C_1 - \frac{(x_2 - x_1)}{(T_1 - T_2)} \frac{J}{D_0} \mu(\tau) , \end{aligned} \quad (63)$$

where

$$\begin{aligned} \mu(\tau) &= \int_{\tau_1}^{\tau} \frac{e^{\frac{(Q_D - \alpha)}{R}\tau}}{\tau^{\frac{\beta}{R} + 2}} d\tau \\ &= \sum_{n=0}^{\infty} \frac{\left(\frac{Q_D - \alpha}{R} \right)^n \left(\tau^{n - \frac{\beta}{R} - 1} - \tau_1^{n - \frac{\beta}{R} - 1} \right)}{n! (n - \frac{\beta}{R} - 1)} . \end{aligned} \quad (64)$$

Then

$$J = \mathbb{D}_0 \frac{(T_1 - T_2)}{(x_2 - x_1)} F_3(C_1 - C_2) , \quad (65)$$

and

$$F_3 = \frac{\frac{e^{-\frac{\alpha}{R}\tau_1}}{\frac{\beta}{R}} C_1 - \frac{e^{-\frac{\alpha}{R}\tau_2}}{\frac{\beta}{R}} C_2}{\frac{\tau_1}{(C_1 - C_2)\mu(\tau_2)}} , \quad (66)$$

$$R = \frac{(x_2 - x_1)}{\mathbb{D}_0 (T_1 - T_2) F_3} , \quad (67)$$

and

$$J = \int_A J dA . \quad (68)$$

The preceding is based on the assumption that β/R is not an integer. Instances in which β/R is an integer should be rare. Practical details of the computation of the series in Eq. (64) are discussed in Appendix C.

Cylindrical shell. For a cylindrical shell the corresponding results are

$$J_{\theta L} = rJ = - \mathbb{D}_0 e^{-\frac{Q_0}{RT}} r \left[\frac{dC}{dr} + \left(\frac{\alpha}{RT^2} + \frac{\beta}{RT} \right) \frac{dT}{dr} C \right] = \text{constant} , \quad (69)$$

$$\frac{e^{-\frac{\alpha}{R}\tau}}{\frac{\beta}{R}} C = \frac{e^{-\frac{\alpha}{R}\tau_1}}{\frac{\beta}{R}} C_1 + \frac{\ln(r_2/r_1)}{(T_1 - T_2)} \frac{J}{\mathbb{D}_0} \mu(\tau) , \quad (70)$$

$$J_{\theta L} = \mathbb{D}_0 \frac{(T_1 - T_2)}{\ln(r_2/r_1)} F_3(C_1 - C_2) , \quad (71)$$

$$R = \frac{\ln(r_2/r_1)}{\mathbb{D}_0 (T_1 - T_2) F_3} , \quad (72)$$

and

$$J = \theta \int_0^L J dl . \quad (73)$$

Spherical shell. Similarly, for a spherical shell

$$J_{\Omega} = r^2 J = - D_0 e^{-\frac{Q_D}{RT}} r^2 \left[\frac{dC}{dr} + \left(\frac{\alpha}{RT^2} + \frac{\beta}{RT} \right) \frac{dT}{dr} C \right] = \text{constant}, \quad (74)$$

$$\frac{e^{-\frac{\alpha}{R} \tau}}{\frac{\beta}{\tau R}} C = \frac{e^{-\frac{\alpha}{R} \tau_1}}{\frac{\beta}{\tau_1 R}} C_1 + \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \frac{J_{\Omega}}{D_0} \mu(\tau) , \quad (75)$$

$$J_{\Omega} = D_0 \frac{(T_1 - T_2) r_1 r_2}{(r_2 - r_1)} F_3(C_1 - C_2) , \quad (76)$$

$$R = \frac{(r_2 - r_1)}{D_0 (T_1 - T_2) r_1 r_2 F_3} , \quad (77)$$

and

$$J = \int_{\Omega} J_{\Omega} dw . \quad (78)$$

V. TRAPPING OF DIFFUSING HYDROGEN-ISOTOPE ATOMS IN METALS BY CHEMICAL REACTION WITH IMPURITIES AND BY COLLECTION AT GRAIN BOUNDARIES AND LATTICE IMPERFECTIONS

The following is a modest extension of an analysis by McNabb and Foster³ for trapping of hydrogen by potential wells in iron and steels. Assume that there exist within the barrier metal in small concentrations a number of different kinds of "sites", e.g., chemical-impurity atoms or lattice imperfections, such as dislocations and grain boundaries, which are capable of combining with or trapping diffusing hydrogen-isotope atoms. Let the specific (per unit volume) rate of capture of atoms of diffusing hydrogen isotope by a site of Type i be proportional to the product of the concentration of the diffusing hydrogen isotope raised to an arbitrary power, equal to the number of atoms which occupy that type of site, and to the concentration of sites of that type.

Where significant temperature dependence appears likely, it will be specifically indicated. Thus, the rate is assumed to be given by

$$n_i k_{1i}(T) C_D^{n_i} C_{S_i}(T) (1 - f_i), i = 1, \dots, I. \quad (79)$$

Similarly, let the specific (per unit volume) rate of release of hydrogen atoms from a site of Type i be proportional to the concentration of occupied sites of that type

$$n_i k_{2i}(T) C_{S_i}(T) f_i, i = 1, \dots, I. \quad (80)$$

Let us assume for the present that the concentrations of sites of each type are not direct functions of time, i.e., that concentrations change with time only if heat transfer is nonsteady. Activation and/or deactivation of sites owing to changes in temperature are represented by the dependences of concentrations of sites and rate constants on temperature.

A balance on an arbitrary volume of fixed position and geometry for all atoms of a particular isotope of hydrogen, trapped plus diffusing, may be expressed in the form:

$$\{\text{net rate of accumulation of trapped and diffusing hydrogen atoms in arbitrary volume}\} + \{\text{net rate of diffusion of hydrogen atoms from arbitrary volume}\} = 0. \quad (81)$$

The first term may be written as

$$\frac{d}{dt} \left\{ \iiint_V \left[C_D + \sum_{i=1}^I n_i C_{S_i}(T) f_i \right] dV \right\} \quad (82)$$

and, because the volume is fixed in location, size, and shape, may also be written as:

$$\iiint_V \frac{\partial}{\partial t} \left[C_D + \sum_{i=1}^I n_i C_{S_i}(T) f_i \right] dV. \quad (83)$$

The diffusion term may be expressed as

$$\int_S \vec{J}(T) \cdot d\vec{S} \quad (84)$$

and transformed, as using the Gauss divergence theorem, to

$$\iiint_V [\nabla \cdot \vec{J}(T)] dV . \quad (85)$$

Combination of the two preceding expressions then gives

$$\iiint_V \frac{\partial}{\partial t} \left\{ C_D + \sum_{i=1}^I n_i C_{S_i}(T) f_i \right\} + \nabla \cdot \vec{J}(T) dV = 0 . \quad (86)$$

A similar balance on an arbitrary volume of fixed location and geometry for only atoms of a particular hydrogen isotope, which have been trapped in sites of Type i , may be expressed in the form

$$\{\text{net rate of accumulation of hydrogen isotope atoms trapped by sites of Type } i \text{ in arbitrary volume}\} + \{\text{net rate of transfer of trapped hydrogen isotope atoms from sites of Type } i \text{ to the diffusing hydrogen atom population}\} = 0 , \quad (87)$$

for each Type i of sites. The first term may be written as

$$\frac{a}{dt} \left\{ \iiint_V [n_i C_{S_i}(T) f_i] dV \right\} = \iiint_V \frac{\partial}{\partial t} [n_i C_{S_i}(T) f_i] dV, \quad i = 1, \dots, I, \quad (88)$$

whereas the second term is given by

$$\iiint_V \{ [n_i k_{2_i}(T) C_{S_i}(T) f_i - n_i k_{1_i}(T) C_H^{n_i} C_{S_i}(T) (1 - f_i)] \} dV, \quad i = 1, \dots, I. \quad (89)$$

By virtue of arguments similar to those used to obtain the preceding hydrogen-atom balance, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} [n_i C_{S_i}(T) f_i] + [n_i k_{2_i}(T) C_{S_i}(T) f_i - n_i k_{1_i}(T) C_H^{n_i} C_{S_i}(T) (1 - f_i)] &= 0, \\ i &= 1, \dots, I. \end{aligned} \quad (90)$$

For a discussion of the mathematics of unsteady transport of hydrogen in metals involving trapping at special rates, the reader is referred to the paper by McNabb and Foster.³ Here, however, we are interested only in steady-state transfer. Under steady-state conditions the fundamental equations, i.e., the hydrogen-atom balance equations, reduce to

$$\nabla \cdot \vec{J}(T) = 0 , \quad (91)$$

and

$$f_i = \frac{k_{1i}(T)C_D^{n_i}}{k_{2i}(T) - k_{1i}(T)C_D^{n_i}}, \quad i = 1, \dots, I. \quad (92)$$

These results show that the steady-state flux is independent of hydrogen trapping, regardless of site types or nonuniform temperatures, provided it is assumed that the diffusion coefficient is not affected by the trapped hydrogen loading and that the other listed conditions are fulfilled. For the dilute solutions of interest in thermonuclear reactor design, these assumptions represent good approximations. Under unsteady-state transfer conditions, net transfer between the trapped hydrogen-atom population on the diffusing hydrogen-atom population will, in general, occur, but once steady state is achieved, net transfer between the two populations ceases, with the equilibrium between the two described by the preceding equations. Although other postulates and models are possible, it seems clear that under any reasonable formulation of the problem, a similar conclusion is inevitable.

Therefore, fears which have been expressed concerning the effect of trapping, e.g., by impurities, crystalline lattice imperfections, or grain boundaries on tritium migration in thermonuclear reactor power plants operated substantially at steady state appear groundless. This result is indeed fortunate, because the task of obtaining the physicochemical data needed for an accurate analysis that would take into consideration such effects appears formidable. However, if some mode of substantially cyclic operation, e.g., in terms of concentrations or temperatures, is attempted, such effects may become important.

On the other hand, the total amount of absorbed hydrogen--not of primary interest in this report--does depend on hydrogen trapping even in steady-state operation. While current indications are that hydrogen isotope holdup due to trapping will be a minor consideration, except perhaps for tritium during startup of pioneering reactors, this view may be subject to future alteration. If the necessary physicochemical data are available or can be predicted with sufficient accuracy, the amount of absorbed hydrogen may be obtained, e.g., for a plane barrier, according to

$$m = \int_{x_1}^{x_2} \left[C_D + \sum_{i=1}^I n_i C_{S_i}(T) f_i \right] dx, \quad M = \int_A m da, \quad (93)$$

with an appropriate temperature distribution substituted into the expression for f_i as a function of C_H .

The assumptions of small concentrations of hydrogen-isotope atom trapping sites and the constancy of these concentrations with respect to time at a fixed temperature appear to warrant further discussion. If concentrations of hydrogen isotope trapping sites are sufficiently large, large variations in diffusing-population concentrations, and hence, large variations in trapped-population concentrations, could result in large variations in diffusivities, due to blocking of interstitial pathways for the elementary atomic jumps whose summation constitutes diffusion, by large alterations in crystalline lattice parameters, formation of separate phases, etc. If site concentrations change slowly with time at constant temperature, e.g., increase as a result of cumulative radiation damage in the strong radiation field of the thermonuclear reactor core region, the principal conclusion of this section is still valid but physiochemical property variation of the diffusion system with respect to time, or, equivalently, with respect to cumulative radiation damage, must be included in the analysis.

A final note of warning appears appropriate. The unsteady-state theory of McNabb and Foster³ indicates that experimental values of apparent diffusivity, i.e., ignoring hydrogen trapping effects, obtained from measurements of unsteady desorption of hydrogen from metal samples will be lower than the true diffusivity, and vice versa for unsteady absorption experiments, if trapping effects are of significant magnitudes. These facts are readily appreciated if the hydrogen trapping sites are viewed as (1) sinks, increasing diffusing hydrogen atom concentration gradients, but not analyzed total gradients, for unsteady absorption; and (2) sources, decreasing diffusing hydrogen atom concentration gradients, but not analyzed total gradients, for unsteady desorption. Thus, in Case (1) the flux-total concentration-gradient ratio is larger than the flux-diffusing species concentration-gradient ratio, while in Case (2) the opposite is true. Therefore, diffusivity values obtained from unsteady-state experiments should be viewed with some caution.

However, diffusivity data for hydrogen in iron and steels collected by McNabb and Foster³ indicate that as temperature increases, trapping becomes less effective and apparent diffusivities are less affected by trapping. Thus high-temperature values are less suspect on this account.

VI. VALIDITY OF SIEVERTS' LAW FOR SOLUBILITY OF INDIVIDUAL HYDROGEN ISOTOPES IN METALS AND IMPLICATIONS FOR SOLUTIONS OF MIXED HYDROGEN ISOTOPES IN METALS

The only explicit considerations of the problem of predicting solubilities of the individual isotopes in a mixture of hydrogen isotopes in metals and the problem of predicting the gross solubility of the mixture in metals which have come to the author's attention are those of Hickman¹⁹ and Ackerman and Koskinas.²⁰ Hickman suggested that protium and deuterium should be viewed as the same chemical species, that a mixture of these two isotopes be treated as a single chemical species, and that at low concentrations a mixture Sieverts'-law relationship would be appropriate:

$$N_{\text{Total}} = K_{S_{\text{Total}}}(T) P_{\text{Total}}^{1/2} \quad (94)$$

He further suggested the simple linear mixing rule:

$$K_{S_{\text{Total}}}(T) = y_{H_2} K_{S_H}(T) + y_{D_2} K_{S_D}(T) \quad (95)$$

Note that here the vapor-phase mole fractions are those determining the gross isotopic ratio. He reasoned that only a limited number of holes in the valance bond of a metal is available for accepting electrons during dissolution of gas molecules and that both isotopes must compete for the same holes.

Hickman then obtained experimental data for the solubility of a 50:50 mol% mixture of protium and deuterium in a 75:25 mol% alloy of palladium and silver. The results led to the conclusion that the postulated mixing rule described the solubility of the isotopic mixture acceptably well. In particular, that the suggested combining rule predicts gross mixture solubilities intermediate to the solubilities of the individual isotopes at partial pressures equal to partial pressure of the mixture as a whole and that his data are in agreement with this prediction. Note that his data were obtained for relatively high concentrations of dissolved isotopes, ~ 0.02 atom fractions and higher.

Ackerman and Koskinas, who used the mixing rule suggested by Hickman in analyzing the results of experiments on the permeation of mixtures of protium and deuterium through the walls of 75Pd-25Ag tube, suggested that individual isotopic solubilities could be estimated according to

$$\frac{N_{H(s)}}{N_{D(s)}} = \frac{y_{H_2} K_{S_H}(T)}{y_{D_2} K_{S_D}(T)} \quad (96)$$

The agreement between theory based upon the mixing rule of Hickman and this postulate and their experimental permeation data appears to be quite good. However, once again high dissolved-hydrogen-isotope concentrations were involved. On the other hand, these investigators obtained data indicating that for the solubilities of protium and deuterium up to quite high concentrations, Sieverts' law represented a good approximation.

An alternative theory of mixed hydrogen isotope solubility can be based on the postulate that the individual isotopes behave as independent species. The validity of Sieverts' law for solubility of gases in metals at low concentrations has certain implications for the solubility of mixtures of hydrogen isotopes in dilute solution in metals which are, at least apparently, at variance with the suggested mixing rule of Hickman. Therefore, the rest of this section is devoted to an examination of approximations and postulates involved in the formulation of Sieverts' law, to a discussion of the implications that Sieverts' law is valid for the solubility of hydrogen-isotope mixtures in metals, and to a discussion of the relationship between Hickman's mixing rule and a mixing rule based on the implications of Sieverts' law.

A set of postulates and approximations leading to Sieverts' law will be examined first. Consider the equilibrium for the chemical reaction

between gaseous diatomic molecules and dissociated atoms of a single hydrogen isotope, say protium, dissolved in a metal. The equilibrium constant may be expressed in the form

$$\frac{f_{H(s)} / f_{H(s)}^\circ(p, T)}{f_{H_2(g)}^{1/2} / \text{atm.}^{1/2}} = K_{EQ_H}(T) = e^{-\frac{\Delta G_H^\circ(T)}{RT}} = e^{-\frac{\left[\bar{g}_{H(s)}^\circ(T) - \frac{1}{2} \bar{g}_{H_2(g)}^\circ(T) \right]}{RT}}, \quad (98)$$

if it is assumed that the free-energy change for the host metal, and hence its fugacity, are not altered significantly by this dissolution. This approximation does not appear unreasonable for sufficiently dilute solutions.

At low pressures

$$f_{H_2(g)} \approx p_{H_2} = y_{H_2} p_{\text{Total}} \quad (99)$$

By definition

$$f_{H(s)} / f_{H(s)}^\circ(p, T) = \gamma_{H(s)} [p, T, x_{H(s)}] x_{H(s)} \quad (100)$$

For sufficiently dilute solutions $x_{H(s)}$ differs negligibly from $N_{H(s)}$ and therefore

$$f_{H(s)} / f_{H(s)}^\circ(p, T) \approx \gamma_{H(s)} [p, T, N_{H(s)}] N_{H(s)} \quad (101)$$

At low pressures, because $\gamma_{H(s)}$ is associated with a condensed phase, its dependence on pressure will generally be negligible

$$f_{H(s)} / f_{H(s)}^\circ(p, T) \approx \gamma_{H(s)} [T, N_{H(s)}] N_{H(s)} \quad (102)$$

Now

$$\Delta G_H^\circ(T) = \Delta H_H^\circ(T) - T \Delta S_H^\circ(T) \quad (103)$$

and therefore

$$K_{EQ_H}(T) = e^{\frac{\Delta S_H^\circ(T)}{R}} e^{-\frac{\Delta H_H^\circ(T)}{RT}} \quad (104)$$

But the variation of $[\Delta S_H^\circ(T)]/R$ with temperature is usually modest and the large rate of variation of $[\Delta H_H^\circ(T)]/RT$ with temperature for even modest values of $\Delta H_H^\circ(T)$ generally completely masks that of $[\Delta S_H^\circ(T)]/R$. Thus the approximation

$$K_{EQ_H}(T) \approx K_{EQ_H}^\circ e^{-\frac{\Delta H_H^\circ(T)}{RT}} \quad (105)$$

is often employed in analyses both theoretical and of experimental data.

Combination of the preceding results gives

$$p_{H_2(g)}^{1/2} \approx \frac{1}{K_{EQ_H}^\circ} e^{\frac{\Delta H_H^\circ(T)}{RT}} \gamma_{H(s)} [T, N_{H(s)}] N_{H(s)} \quad (106)$$

But Sieverts' law is

$$P_{H_2}^{1/2}(g) = \frac{1}{K_{S_H}^0} e^{\frac{Q_{S_H}}{RT}} N_{H(s)} \quad (107)$$

Comparison between these last two equations reveals that Sieverts' law implies that

$$\gamma_{H(s)}[T, N_{H(s)}] \approx 1, \quad (108)$$

and further that

$$\Delta H_H^0(T) \approx \Delta H_H^0, \quad (109)$$

i.e., that the temperature dependence of the heat of solution may be neglected.

An activity coefficient of unity for the solute implies a certain simplicity for the solution, i.e., that the solution is ideal or that the solute obeys Henry's law. Ideal solution behavior is not expected to be even a useful approximation. Solution components are too dissimilar. There is also a large body of experimental evidence supporting this view, e.g., heats of solution are not zero, and in fact are large, Sieverts' law constants depend on the host-metal properties, etc., even when referred to the dissociated atoms. On the other hand, Henry's law is usually found to be obeyed by solutes in sufficiently dilute solutions and the concentration region of interest with regard to thermonuclear reactor design is, of course, that of dilute solutions of hydrogen isotopes.

One important property of solutions in which the solutes obey Henry's law is that the solvent properties are those of a component in an ideal solution, e.g., the solvent fugacity is given by a standard-state fugacity, that of the pure solvent at the same temperature and pressure, multiplied by its mole fraction, which, for sufficiently dilute solutions, differs negligibly from unity. In solutions sufficiently dilute in all solutes, solute atoms are surrounded by and interact virtually all the time with solvent atoms, rather than with other solute atoms. Therefore, in such solutions, the solubility of any one solute is determined primarily by its properties and those of the solvent and is affected negligibly by the properties of other solutes. This interpretation is also applicable if the solvent is a mixture of species, as

long as the ratios of concentrations of the species comprising the solvent remain constant, i.e., the same remarks apply if the host metal is an alloy, dilute or otherwise.

Thus, the conclusion is that Sieverts'-law expressions obtained by fitting experimental data obtained from solubility determinations for pure isotopes are applicable to individual isotope solubilities when isotopic mixtures are involved:

$$N_{H(s)} = K_H^\circ e^{\frac{Q_{S_H}}{RT}} p_{H_2}^{1/2} = K_H^\circ e^{\frac{Q_{S_H}}{RT}} y_{H_2}^{1/2} p_{Total}^{1/2} \approx f_{H(s)} / f_{H(s)}^\circ, \quad (110)$$

$$N_{D(s)} = K_D^\circ e^{\frac{Q_{S_D}}{RT}} p_{D_2}^{1/2} = K_D^\circ e^{\frac{Q_{S_D}}{RT}} y_{D_2}^{1/2} p_{Total}^{1/2} \approx f_{D(s)} / f_{T(s)}^\circ, \quad (111)$$

and

$$N_{T(s)} = K_T^\circ e^{\frac{Q_{S_T}}{RT}} p_{T_2}^{1/2} = K_T^\circ e^{\frac{Q_{S_T}}{RT}} y_{T_2}^{1/2} p_{Total}^{1/2} \approx f_{T(s)} / f_{T(s)}^\circ. \quad (112)$$

The standard-state fugacities of solutes which obey Henry's law generally depend on solvent properties, as well as on the properties of the solutes, and this is in accord with the empirical fact that the constants in Sieverts' law are generally observed to be different for different host metals. An ideal solution standard-state fugacity, on the other hand, is independent of the properties of other species and is a function solely of the properties of the component in question and its mole fraction.

Because of the independence of individual component solutions when in the Sieverts'-law, and hence Henry's-law, regime, the total solubility of the three hydrogen isotopes is obtained by addition of the three individual solubilities:

$$N_{Total} = N_{H(s)} + N_{D(s)} + N_{T(s)} = K_{S_H}^\circ e^{\frac{Q_{S_H}}{RT}} p_{H_2}^{1/2} + K_{S_D}^\circ e^{\frac{Q_{S_D}}{RT}} p_{D_2}^{1/2}$$

$$\begin{aligned}
+ K_{S_T}^{\circ} e^{\frac{Q_{S_T}}{RT}} p_{T_2}^{1/2} &= \left[K_{S_H}^{\circ} e^{\frac{Q_{S_H}}{RT}} y_{H_2}^{1/2} + K_{S_D}^{\circ} e^{\frac{Q_{S_D}}{RT}} y_{D_2}^{1/2} + K_{S_T}^{\circ} e^{\frac{Q_{S_T}}{RT}} y_{T_2}^{1/2} \right] p_{Total}^{1/2} \\
&= \left[K_{S_H(T)} y_{H_2}^{1/2} + K_{S_D(T)} y_{D_2}^{1/2} + K_{S_T(T)} y_{T_2}^{1/2} \right] p_{Total}^{1/2} = K_{S_{Total}(T)} p_{Total}^{1/2} . \quad (113)
\end{aligned}$$

The last form would appear to have its greatest utility if p_{Total} is taken as the sum of the partial pressures of the hydrogen isotopes rather than as the sum of the partial pressures of the hydrogen isotopes plus any other gaseous species present.

The mixing rule just derived, which is based on an assumption of individual action of the isotopic species, has one mathematical property that immediately renders it qualitatively different from the mixing rule of Hickman. According to this alternative mixing rule, the solubility of the mixture can exceed that of its most soluble component when the partial pressure of that component is set equal to that of the mixture as a whole. If the various isotopic species do indeed act as completely independent chemical species at sufficiently low concentrations, then this property of the alternative mixing rule is not physically unrealistic. In particular, for the 50:50 mol% protium-deuterium mixture examined by Hickman, the alternative mixing rule would predict a gross mixture solubility greater than that of the more soluble protium at the partial pressure of the mixture as a whole.

An obvious question is: Can these conflicting theories be reconciled? One possible hypothesis is that the concentrations of conduction-band holes of the host metal are very low and that these holes essentially comprise the solvent substance so that the solution of hydrogen isotopes is not truly dilute under the conditions being considered. However, the apparent validity of Sieverts' law for individual hydrogen-isotope solubility in 75Pd-25Ag alloy up to rather high concentrations argues against this view.

It does appear, however, that these previous investigators have overlooked the following facts, which have also not yet been introduced into the alternative theory. A mixture of hydrogen and deuterium in the gas phase, will undergo isotopic exchange with the result that at equilibrium, rapidly attained at high temperature, the isotopic mixture will consist roughly of 50 mol% DH and 25 mol% each of H_2 and D_2 if the mixture initially consisted of 50 mol% H_2 and 50 mol% D_2 . This follows from the fact that at high temperatures

$$K_{HD} = \frac{p_{HD}^2}{p_{H_2} p_{D_2}} \approx 4, \quad (114)$$

e.g., see Table III. A value of 4 for K_{HD} is the high-temperature limit. At such temperatures and the high pressures used by Hickman²⁰ and by Ackerman and Koskinas,²¹ dissociation of H_2 , D_2 , and HD to produce protium and deuterium atoms may be neglected according to the values of the dissociation constants listed in Table III. The temperature at which Hickman obtained his data was 300°C or 573K for which K_{HD} is ~ 3.7 . Furthermore, Sieverts' law represents an equilibrium relationship between a nondissociated hydrogen isotope molecule and dissolved hydrogen isotope atoms and is independent of the presence of the HD .

Now consider a 50:50 mol% isotopic mixture of protium and deuterium. According to Hickman's mixing rule, which ignores dissociation, one has

$$K_{S_{Total}}(T) = 0.5 K_{S_H}(T) + 0.5 K_{S_D}(T). \quad (115)$$

On the other hand, with

$$K_{HD}(T) \approx 4 \quad (116)$$

so that

$$y_{H_2} \approx 0.25, y_{D_2} \approx 0.25 \quad (117)$$

one has, using the alternative mixing rule developed herein and taking dissociation into account

$$K_{S_{Total}}(T) \approx (0.25)^{1/2} K_{S_H}(T) + (0.25)^{1/2} K_{S_D}(T) = 0.5 K_{S_H}(T) + 0.5 K_{S_D}(T). \quad (118)$$

The data of Hickman do not appear to be sufficiently precise to allow a choice to be made between the two theories, which would apparently have to be based on detecting a small deviation of the value of K_{HD} from 4. His data are simply not sufficient to provide convincing experimental support for his hypothesis because the scatter of his data, apparently of the order of a few percent, is too great. For example, at 500 K, less than the 572.3 K at which his measurements were obtained and for which the value of K_{HD} would be even closer to 4, the value of K_{HD} is 3.62, which corresponds to

TABLE III
EQUILIBRIUM CONSTANTS K_{HD} , K_{HT} , AND K_{DT} AND DISSOCIATION CONSTANTS
 K_{H_2} , K_{D_2} , and K_{T_2} AS FUNCTIONS OF TEMPERATURE^a

T, K	$K_{H_2},^b \text{ atm}$	$K_{D_2},^b \text{ atm}$	$K_{T_2},^c \text{ atm}$	K_{HD}^c	K_{HT}^c	K_{DT}^c
300	18.39×10^{-72}	1.319×10^{-72}	---	3.26	2.58	3.82
400	---	---	---	3.48	2.99	3.88
500	4.939×10^{-14}	1.171×10^{-41}	---	3.62	3.26	3.93
600	---	---	---	3.72	3.45	3.96
700	---	---	---	3.78	3.59	3.97
800	---	---	---	3.83	3.68	3.98
900	---	---	---	3.87	3.76	3.98
1000	5.174×10^{-18}	2.972×10^{-18}	3.01×10^{-18}	3.90	3.81	3.99
1250	---	---	---	3.94	3.90	4.00
1500	3.100×10^{-10}	2.330×10^{-10}	2.44×10^{-18}	3.96	3.94	4.00
2000	2.641×10^{-6}	2.227×10^{-6}	2.35×10^{-18}	3.97	3.98	4.00

$$^a \quad K_{H_2} = \frac{p_H^2}{p_{H_2}} ; K_{D_2} = \frac{p_D^2}{p_{D_2}} ; K_{T_2} = \frac{p_T^2}{p_{T_2}} ; K_{HD} = \frac{p_{HD}^2}{p_{H_2} p_{D_2}} ; K_{HT} = \frac{p_{HT}^2}{p_{H_2} p_{T_2}} ;$$

$$K_{DT} = \frac{p_{DT}^2}{p_{D_2} p_{T_2}} .$$

^b Woolley, et al.²²

^c Jones.²³

$$y_{H_2} : y_{D_2} = 0.2563, y_{H_2}^{1/2} = y_{D_2}^{1/2} = 0.5063 \quad (119)$$

for

$$y_{H_2}^{\circ} = y_{D_2}^{\circ} = 0.5 . \quad (120)$$

More generally, if K_{HD} is taken as 4, the high-temperature-limiting value, one has

$$\frac{y_{HD}^2}{y_{H_2}^2 y_{D_2}^2} = \frac{y_{HD}}{\left(y_{H_2}^{\circ} - \frac{y_{HD}}{2}\right)^2 \left(y_{D_2}^{\circ} - \frac{y_{HD}}{2}\right)^2} = 4 , \quad (121)$$

which gives

$$y_{HD} = \frac{2 y_{H_2}^{\circ} y_{D_2}^{\circ}}{y_{H_2}^{\circ} + y_{D_2}^{\circ}} = 2 y_{H_2}^{\circ} y_{D_2}^{\circ} , \quad (122)$$

$$y_{H_2} = y_{H_2}^{\circ} - y_{H_2}^{\circ} y_{D_2}^{\circ} = y_{H_2}^{\circ} - y_{H_2}^{\circ} (1 - y_{H_2}^{\circ}) = y_{H_2}^{\circ 2} , \quad (123)$$

and

$$y_{D_2} = y_{D_2}^{\circ 2} \quad (124)$$

for

$$y_{H_2}^{\circ} + y_{D_2}^{\circ} = 1 , \quad (125)$$

provided dissociation to form atomic species is negligible. Then, according to Hickman's suggested combining rule,

$$K_{S_{Total}}(T) = y_{H_2}^{\circ} K_{S_H}(T) + y_{D_2}^{\circ} K_{S_D}(T) \quad (126)$$

and according to the mixing rule resulting from the implications of validity of Sieverts' law

$$K_{S_{Total}}(T) = y_{H_2}^{1/2} K_{S_H}(T) + y_{D_2}^{1/2} K_{S_D}(T) = y_{H_2}^{\circ} K_{S_H}(T) + y_{D_2}^{\circ} K_{S_D}(T) . \quad (127)$$

Even more generally, if K_{HT} , K_{HD} , and K_{DT} are all taken as equal exactly to 4, their high-temperature-limiting values, it is easily shown that after equilibration

$$y_{H_2} = y_{H_2}^{\circ 2}, y_{D_2} = y_{D_2}^{\circ 2}, y_{T_2} = y_{T_2}^{\circ 2}, \quad (128)$$

and once again the result is that both approaches yield the same value for the isotopic-mixture Sieverts'-law constant, regardless of the values of the isotopic ratios. It is therefore apparent that whether or not Hickman's approach to the problem is correct or not, his mixing rule represents a useful approximation.

Furthermore, the statement of Ackerman and Koskinas that permeation of mixtures of protium and deuterium through 75Pd-25Ag alloy is not affected by isotopic exchange in the gas phase does not appear warranted. This claim was made on the basis that diffusion through such barriers occurs by an atomic mechanism rather than by diffusion of molecular species. However, the atomic species at the barrier faces, which determine the overall driving force for diffusion through the barrier, are believed to be determined largely by equilibrium solubility relationships under the experimental conditions of Ackerman and Koskinas. These investigators also examined only the permeation of 50:50 mol% mixtures of protium and deuterium.

If temperatures are sufficiently high or partial pressures sufficiently low, dissociation to form atomic species in the gas phase cannot be neglected. In the general case, i.e., nonnegligible dissociation and all three isotopic species present, a large number of equilibrium relations, e.g.,

$$K_{HD}(T) = \frac{p_{HD}^2}{p_{H_2} p_{D_2}}, K_{HT}(T) = \frac{p_{HT}^2}{p_{H_2} p_{T_2}}, K_{DT}(T) = \frac{p_{DT}^2}{p_{D_2} p_{T_2}}, \quad (129)$$

and

$$K_{H_2}(T) = \frac{p_H^2}{p_{H_2}}, K_{D_2}(T) = \frac{p_D^2}{p_{D_2}}, K_{T_2}(T) = \frac{p_T^2}{p_{T_2}}, \quad (130)$$

must be solved to obtain partial pressures for the various species. Other chemical equilibria involving the hydrogen isotopes may also have to be

considered. Clearly, efficient numerical techniques for solution of the complex equilibrium will be necessary in such instances.

Note that no conflict exists between the approach of Hickman and that suggested by the implications of validity of Sieverts' law to formulation of a mixing rule if solubilities are expressed in terms of equilibria between atomic species in both the gas and the metal phases. Equilibrium between atomic species in the gas and solid phases may be expressed in the form

$$N_{H(s)} = K_H(T)p_H, N_{D(s)} = K_D(T)p_D, N_{T(s)} = K_T(T)p_T, \quad (131)$$

where

$$K_H(T) = \frac{K_{S_H}(T)}{K_{H_2}(T)}, K_D(T) = \frac{K_{S_D}(T)}{K_{D_2}(T)}, K_T(T) = \frac{K_{S_T}(T)}{K_{T_2}(T)}. \quad (132)$$

Both Hickman's approach and the alternative approach then result in the mixing rule:

$$K_{Total}(T) = y_H K_H(T) + y_D K_D(T) + y_T K_T(T) \quad (133)$$

to be used in

$$N_{Total} = K_{Total}(T) (p_H + p_D + p_T). \quad (134)$$

VII. DISCUSSION

Equations useful for the design of thermonuclear reactor systems with respect to tritium leakage and recovery for recycling have been derived for nonisothermal conditions. The relations for the fluxes of hydrogen isotopes through metal barriers developed in Secs. III and IV are believed to be commensurate in accuracy with current knowledge of ordinary and thermal diffusion of hydrogen isotopes through metals and with available thermophysical property data. The assumptions of constant thermal conductivity and quasi-unidirectional heat transfer used in the base cases analyzed in this report should not constitute significant sources of inaccuracy, particularly not at the present stage of thermonuclear reactor design. By restricting ourselves to only plane, cylindrical shell, and spherical shell barriers we did not severely limit the usefulness of the results developed herein for design purposes. More

complex geometries can probably be analyzed with acceptable accuracy by representing them as composites of these geometrical elements.

The results presented in Tables I and II and in the sample calculations of Appendix C demonstrate clearly that the errors introduced into analyses of tritium migration in thermonuclear reactor systems by neglecting the effects of large temperature gradients through metal components on thermophysical properties and by neglecting thermal diffusion can be significant. Experimental data on the temperature dependences of many thermophysical properties are generally available for many construction materials currently considered for use in thermonuclear reactor systems, so that no serious difficulty should arise in introducing such considerations into tritium migration analyses. However, experimental values for heats of transport are scarce, and accurate predictive methods for heats of transport for hydrogen isotopes through metals, especially as functions of temperature, required for estimation of thermal diffusion fluxes in the absence of experimental data, are not available. The scarcity of heat-of-transport data is one of the most serious obstacles to widespread application of thermal-diffusion theory to thermonuclear reactor systems analysis and design. However, the limited data do suggest that the temperature dependences of heats of transport may be represented with acceptable accuracy over wide temperature ranges by means of linear functions of temperature.

Information useful for the formulation of efficient and accurate computer programs for numerical evaluation of the theoretical formulae presented in this report were presented in Appendix C. Details of alterations of the base-case analyses to take into consideration the significant dependence of thermal conductivity on temperature and the dependence on temperature of heat of transport stronger than first degree are discussed in Appendices A and D, respectively. The computation of the amounts of diffusing hydrogen isotopes contained in a barrier is examined in Appendix A. Some discussion, together with references to other sources of information, concerning various mechanisms that might affect the validity of the results derived herein are also presented.

The results of the generalized analysis of trapping of diffusing hydrogen isotopes by chemical reactions with impurities and collection at grain boundaries and lattice imperfections of Sec. V indicate that trapping represents a significant influence on transfer rates only under unusual circumstances

for steady state. Therefore we recommend that trapping of diffusing hydrogen isotopes be eliminated from consideration as a significant influence on tritium migration rates in thermonuclear reactors for steady-state operating conditions except under the unusual circumstances mentioned. The theoretical investigation in Sec. VI of mixing rules for dilute dissolution of hydrogen isotope mixtures when Sieverts' law of solubility is applicable demonstrates the approximate equivalence of an empirical mixing rule which has been tested experimentally and a theoretical mixing rule based on a specified set of postulates. The result is increased confidence in the accuracy of the theoretical mixing rule, which we recommend for calculation of hydrogen isotope mixture solubility in metals for design purposes.

APPENDIX A

OUTLINE OF THE ANALYSIS WHEN TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY IS TAKEN INTO CONSIDERATION

Because thermal conductivities of metals usually vary slowly with temperature, their temperature dependences can usually be represented with reasonable accuracy over moderate temperature ranges by linear functions of temperature:

$$k = \phi + \psi T .$$

If, for example, one is concerned with spherical shell geometry, Fourier's law:

$$q = - k \frac{dT}{dr}$$

gives

$$q^* = r^2 q = - (\phi + \psi T) r^2 \frac{dT}{dr} = \text{constant} ,$$

which is easily integrated to obtain the steady-state temperature distribution and heat flux through the barrier:

$$\phi(T - T_1) + \frac{\psi}{2} (T^2 - T_1^2) = \frac{\left[\phi + \psi \left(\frac{T_1 + T_2}{2} \right) \right] [T_1 - T_2] [r_1 r_2]}{[r_2 - r_1]} \left[\frac{1}{r} - \frac{1}{r_1} \right],$$

$$q^* = \frac{\left[\phi + \psi \left(\frac{T_1 + T_2}{2} \right) \right] [T_1 - T_2] [r_1 r_2]}{[r_2 - r_1]} .$$

Substitution into the expression for the combined ordinary and thermal diffusion flux, Eq. (56) of the main body of the report, with heat of transport linearly dependent upon temperature and spherical geometry, results in:

$$J_{\Omega} = \left\{ -D_0 \frac{\left[\phi + \psi \left(\frac{T_1 + T_2}{2} \right) \right] [T_1 - T_2] [r_1 r_2]}{[r_2 - r_1]} \right\} \left\{ \frac{-\frac{Q_D}{RT}}{(\phi + \psi T)} \left[\frac{dC}{dT} + \left(\frac{\alpha}{RT^2} + \frac{\beta}{RT} \right) C \right] \right\}.$$

The substitution

$$T = \frac{1}{\tau}$$

gives

$$\frac{dC}{d\tau} - \left(\frac{\alpha}{R} + \frac{\beta}{R\tau} \right) C = - \left\{ \frac{[r_2 - r_1]}{\left[\phi + \psi \left(\frac{T_1 + T_2}{2} \right) \right] [T_1 - T_2] [r_1 r_2]} \frac{J_{\Omega}}{D_0} \right\} \frac{(\phi\tau + \psi) e^{\frac{Q_D}{R}\tau}}{\tau^3},$$

which has the solution

$$\frac{e^{\frac{\alpha}{R}\tau}}{\tau^{\frac{\beta}{R}}} C = \frac{e^{\frac{\alpha}{R}\tau_1}}{\tau_1^{\frac{\beta}{R}}} C_1 + \frac{[r_2 - r_1]}{\left[\phi + \psi \left(\frac{T_1 + T_2}{2} \right) \right] [T_1 - T_2] [r_1 r_2]} \frac{J_{\Omega}}{D_0} \int_{\tau_1}^{\tau_2} \frac{(\phi\tau + \psi) e^{\frac{Q_D}{R}\tau}}{\tau^{\frac{\beta}{R} + 3}} d\tau .$$

As comparison with Eqs. (64), (66), and (75) of the main body of the report reveals, introduction of linear temperature dependence of thermal conductivity into the analysis does not further complicate the analysis significantly. In fact, analysis with thermal conductivity represented by a polynomial of any degree in temperature introduces no significant new difficulties.

APPENDIX B

COMPUTATION OF ABSORBED HYDROGEN ISOTOPE CAPACITY OF NONISOTHERMAL METAL BARRIERS DURING DYNAMIC TRANSFER

As noted in Sec. II of the main body of this report, the computation of the amount of a hydrogen isotope absorbed in a thin, hot metal barrier will probably be of lesser interest than the flux through the barrier because, in general, the amounts absorbed will be small compared to the total reactor-system inventory. Therefore, the analysis for the absorptive capacity of a nonisothermal barrier will be sketched only briefly. Note, first, that we are not considering the capacity of a large amount of absorbent material introduced to remove hydrogen isotopes from, say, a circulating stream of liquid, e.g., from a lithium or lithium-containing-salt tritium-breeding blanket or coolant loop, or gas, i.e., from a helium coolant loop, with essentially isothermal equilibrium conditions prevailing. Rather, we are concerned here with the capacity of a thin barrier, representing a minor portion of the total absorptive capacity of the system, through which hydrogen isotopes are diffusing, with concentration of absorbed material determined by the transport process rather than by equilibrium considerations. Therefore, one cannot compute the hydrogen isotope holdup in the barrier by simply integrating the temperature-dependent equilibrium solubility over the barrier thickness using the temperature distributions developed in Sec. III. Instead, the expressions derived for the dynamic concentration profiles must be integrated over the barrier thicknesses. Thus, for plane barriers

$$m = \int_{x_1}^{x_2} C \, dx, \quad M = \int_A m \, da ;$$

for cylindrical shells,

$$m_{\theta L} = \int_{r_1}^{r_2} C \, r dr, \quad M = \int_0^L \theta \, m_{\theta L} \, d\theta ;$$

and for spherical shells,

$$m_{\Omega} = \int_{r_1}^{r_2} C r^2 dr, \quad M = \int_{\Omega} m_{\Omega} d\omega.$$

Consider, e.g., the case of a spherical shell with thermal diffusion, with heat of transport a linear function of temperature, as well as temperature dependence of the mass diffusivity taken into consideration. For this case Eqs. (75) and (64) of the main body of this report are applicable and solution for concentration gives

$$C = \left(\frac{\tau}{\tau_1}\right)^{\frac{\beta}{R}} e^{\frac{\alpha}{R}(\tau - \tau_1)} C_1 - (C_1 - C_2) F_3 \tau^{\frac{\beta}{R}} \sum_{n=0}^{\infty} \frac{\left(\frac{Q_D - \alpha}{R}\right)^n \left(\tau^{n - \frac{\beta}{R} - 1} - \tau_1^{n - \frac{\beta}{R} - 1}\right)}{n! (n - \frac{\beta}{R} - 1)}.$$

According to Eq. (12) of the main body of this report

$$r^2 dr = - \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \frac{dT}{\left[\frac{(r_2 - r_1)(T - T_1)}{(T_1 - T_2) r_1 r_2} + \frac{1}{r_1} \right]^4},$$

and with the transformation

$$T = \frac{1}{\tau},$$

one has

$$r^2 dr = \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \frac{\tau^2 d\tau}{\left[\frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} + \left\{ \frac{1}{r_1} - \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \right\} \tau \right]^4}.$$

Thus,

$$m_{\Omega} = \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \frac{e^{-\frac{\alpha}{R} \tau_1}}{\tau_1^{\frac{\beta}{R}}} C_1 \int_{\tau_1}^{\tau_2} \frac{\tau^{\frac{\beta}{R} + 2} e^{\frac{\alpha}{R} \tau}}{\left[\frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} + \left\{ \frac{1}{r_1} - \frac{(r_2 - r_1)}{(T_1 - T_2) r_1 r_2} \right\} \tau \right]^4} d\tau$$

$$- \frac{(r_2 - r_1)(C_1 - C_2)F_3}{(T_1 - T_2)r_1r_2} \int_{\tau_1}^{\tau_2} \frac{\tau^{\frac{\beta}{R} + 2} e^{\frac{\alpha}{R}\tau} \sum_{n=0}^{\infty} \frac{\left(\frac{Q_0 - \alpha}{R}\right)^n \left(\tau^{n - \frac{\beta}{R} - 1} - \tau_1^{n - \frac{\beta}{R} - 1}\right)}{n! (n - \frac{\beta}{R} - 1)}}{\left[\frac{(r_2 - r_1)}{(T_1 - T_2)r_1r_2} + \left\{ \frac{1}{r_1} - \frac{(r_2 - r_1)}{(T_1 - T_2)r_1r_2} \right\} \tau \right]^4} d\tau.$$

Analytic integration in this case appears to be significantly more difficult than is the case for the expression for the flux. Apparently, a double infinite series or an infinite series whose terms are finite series, with finite-series length increasing with infinite-series term number, or numerical integration are involved unless a satisfactory approximate expression for the integral can be found.

APPENDIX C

EFFICIENT COMPUTATION OF FLUXES AND NUMERICAL EXAMPLES

The function $E_1(z)$ may be efficiently computed with acceptable accuracy by using the following rational and polynomial approximations suggested in the System/360 Scientific Subroutine Package:²⁴

$$(1) \quad z \geq 1: \quad ze^z E_1(z) = (z^4 + 8.5733287401 z^3 + 18.0590169730 z^2 + 8.6347608925 z + 0.2677737343) / (z^4 + 9.573322345 z^3 + 25.6329561487 z^2 + 21.09965330827 z + 3.9584969228) + \epsilon,$$

$$|\epsilon| < 2 \times 10^{-8}$$

$$(2) \quad -3 \leq z \leq 1: \quad [E_1(z) + \ln|z| + \sigma]/z = 9.999999 \times 10^{-1} - 2.500001 \times 10^{-1} z + 5.555682 \times 10^{-2} z^2 - 1.041576 \times 10^{-2} z^3 + 1.664156 \times 10^{-3} z^4 - 2.335379 \times 10^{-4} z^5 + 2.928433 \times 10^{-5} z^6 - 1.766345 \times 10^{-6} z^7 + 7.122452 \times 10^{-7} z^8 + \epsilon,$$

$$|\epsilon| < 7.3 \times 10^{-8}$$

$$\sigma = \text{Euler's constant} = 0.5772156649$$

$$(3) \quad -9 \leq x \leq -3: \quad ze^z E_1(z) = 1 - (248.6697 + 224.4234 z + 32.43665 z^2 + 3.061037 z^3 + 0.05176245 z^4) / (180.7837 + 22.65818 z + 38.93944 z^2 + 3.995161 z^3 + z^4) + \epsilon, \\ |\epsilon| < 1.3 \times 10^{-7}$$

$$(4) \quad -174 \leq x \leq -9: \quad ze^z E_1(z) = 1 - (674.567029 + 57.4118330 z - 6.05529252 z^2 - z^3) / (1699.06552 + 841.654932 z + 49.3133893 z^2 - 8.01957683 z^3 - 0.999792040 z^4) + \epsilon, \\ |\epsilon| < 3.8 \times 10^{-7}$$

Numerical experiments were performed to determine the number of terms in the series in Eq. (64) of the main body of this report:

$$\sum_{n=0}^{\infty} \frac{\left(\frac{Q_0 - \alpha}{R}\right)^n \left(\tau_2^{n - \frac{\beta}{R} - 1} - \tau_1^{n - \frac{\beta}{R} - 1}\right)}{n! \left(n - \frac{\beta}{R} - 1\right)} \\ = \left(\tau_2^{-\frac{\beta}{R} - 1}\right) \sum_{n=0}^{\infty} \frac{\left(\frac{Q_0 - \alpha}{R} \tau_2\right)^n \left[1 - \left(\frac{\tau_1}{\tau_2}\right)^{n - \frac{\beta}{R} - 1}\right]}{n! \left(n - \frac{\beta}{R} - 1\right)},$$

which must be evaluated to ensure acceptable accuracy for the partial sum. Analytical methods for determining the number of terms that must be evaluated do not appear to result in sharp limits. The results of the numerical experiments are listed in Table C-I. The numerical results suggest the rough guidelines in Table C-II.

To provide numerical examples as illustrations and for checks on computer output, the following representative parameter values were selected:

$$T_1 = 1000 \text{ K}, T_2 = 900 \text{ K}$$

$$x_1 = 0 \text{ cm}, x_2 = 1 \text{ cm}$$

$$r_1 = 2 \text{ cm}, r_2 = 3 \text{ cm}$$

$$Q_0 = 1 \times 10^{-2} \text{ cm}^2/\text{s}$$

TABLE C-I
NUMERICAL EVALUATION OF INFINITE SERIES

$[(Q_0 - \alpha)/R]\tau_2$	τ_1/τ_2	β/R	N	Partial Sum Minus First Term*
50	0.50	49.5	10	1.6393×10^{21}
			20	6.5677×10^{23}
			30	3.7693×10^{24}
			40	4.6768×10^{24}
			50	4.7066×10^{24}
			60	4.7072×10^{24}
			70	4.7072×10^{24}
			80	4.7072×10^{24}
50	0.90	49.5	10	5.9259×10^{10}
			20	5.2667×10^{15}
			30	3.4016×10^{18}
			40	1.0245×10^{20}
			50	4.2037×10^{20}
			60	5.9524×10^{20}
			70	6.1592×10^{20}
			80	6.1554×10^{20}
			90	6.1655×10^{20}
			100	6.1655×10^{20}
			110	6.1655×10^{20}
50	0.95	49.5	10	5.8140×10^9
			20	8.0972×10^{14}
			30	7.8041×10^{17}
			40	3.2645×10^{19}
			50	1.6765×10^{20}
			60	2.6145×10^{20}
			70	2.7489×10^{20}
			80	2.7536×10^{20}
			90	2.7536×10^{20}
			100	2.7536×10^{20}
			110	2.7536×10^{20}
50	0.50	5.5	10	9.3117×10^9
			20	4.9972×10^{14}

TABLE C-I (Continued)

$[(Q_0 - \alpha)/R]\tau_2$	τ_1/τ_2	β/R	N	Partial Sum Minus First Term*
50	0.95	5.5	30	3.7337×10^{17}
			40	1.4501×10^{19}
			50	7.3832×10^{19}
			60	1.1600×10^{20}
			70	1.2230×10^{20}
			80	1.2253×10^{20}
			90	1.2253×10^{20}
			100	1.2253×10^{20}
			10	1.5796×10^9
			20	2.4039×10^4
			30	2.5295×10^{17}
			40	1.1479×10^{19}
			50	6.2888×10^{19}
			60	1.0143×10^{20}
			70	1.0738×10^{20}
			80	1.0761×10^{20}
			90	1.0761×10^{20}
			100	1.0761×10^{20}
20	0.50	49.5	10	4.8030×10^{17}
			20	8.6952×10^{17}
			30	8.7146×10^{17}
			40	8.7146×10^{17}
			50	8.7146×10^{17}
20	0.90	49.5	10	9.7342×10^6
			20	2.7853×10^8
			30	4.0254×10^8
			40	4.0463×10^8
			50	4.0463×10^8
			60	4.0463×10^8
20	0.95	49.5	10	9.2883×10^5
			20	3.7424×10^7
			30	6.0307×10^7

TABLE C-1 (Continued)

$[(Q_D - \alpha)/R]\tau_2$	τ_1/τ_2	β/R	N	Partial Sum Minus First Term*
20	0.50	5.5	40	6.0860×10^7
			50	6.0861×10^7
			60	6.0861×10^7
			70	6.0861×10^7
			10	1.7456×10^6
			20	2.8788×10^7
			30	4.1013×10^7
			40	4.1266×10^7
			50	4.1267×10^7
			60	4.1267×10^7
			70	4.1267×10^7
			10	2.5112×10^5
			20	1.0831×10^7
			30	1.7901×10^7
5.0	0.50	49.5	40	1.8087×10^7
			50	1.8087×10^7
			60	1.8087×10^7
			10	3.7301×10^{14}
			20	3.7304×10^{14}
5.0	0.95	49.5	30	3.7304×10^{14}
			40	3.7304×10^{14}
			10	2.9920×10^1
			20	3.0252×10^1
			30	3.0252×10^1
5.0	0.50	5.5	40	3.0252×10^1
			10	2.7566×10^2
			20	2.7605×10^2
			30	2.7605×10^2
			40	2.7605×10^2
5.0	0.95	5.5	10	7.7780×10^0
			20	7.8697×10^0

TABLE C-I (Continued)

$\frac{[(Q_D - \alpha)/R]\tau_2}{}$	$\frac{\tau_1/\tau_2}{}$	$\frac{\beta/R}{}$	N	Partial Sum Minus First Term*
			30	7.8697×10^0
			40	7.8697×10^0

$$* \sum_{n=1}^N \frac{\left(\frac{Q_D - \alpha}{R}\right)^n \left[1 - \left(\frac{\tau_1}{\tau_2}\right)^n - \frac{\beta}{R} - 1\right]}{n! \left(n - \frac{\beta}{R} - 1\right)}$$

TABLE C-II

RECOMMENDED NUMBER OF TERMS FOR ACCURATE EVALUATION OF SERIES

$\frac{[(Q_D - \alpha)/R]\tau_2}{}$	Recommended Value of N
$20 \lesssim, \gtrsim 50$	$\gtrsim 80$
$5 \lesssim, \gtrsim 20$	$\gtrsim 40$
$\gtrsim 5$	$\gtrsim 20$

$$Q_D = 20\,000 \text{ g-cal/g-at.}$$

$$Q^* = -10\,000 \text{ g-cal/g-at.}$$

$$\alpha = -21\,000 \text{ g-cal/g-at.}$$

$$\beta = 11 \text{ g-cal/g-at. K (corresponds to } Q^* = 10\,000 \text{ g-cal/g-at. @ } 1\,000 \text{ K)}$$

$$C_1 = 1 \times 10^{-6} \text{ g-at./cm}^3$$

$$C_2 = 1 \times 10^{-7} \text{ g-at./cm}^3$$

$$R = 2 \text{ g-cal/g-at. K.}$$

Using Eqs. (1), (2), and (3) of the main body of the report, which do not take into consideration temperature dependence of mass diffusivity or thermal diffusion, one can compute

$$J = 2.4139 \times 10^{-13} \text{ g-at/cm}^2\text{-s}, J_{\theta L} = 5.9534 \times 10^{-13} \text{ g-at/cm-s},$$

$$J_{\Omega} = 1.4483 \times 10^{-12} \text{ g-at/s} ,$$

where the average of the barrier face temperatures, 950 K, has been used to compute the mass diffusivity.

Equations (23) and (26) of the main body of this report combined, respectively, with Eqs. (25), (34), and (39), and the approximations for $E_1(z)$ presented earlier in this appendix yield the results:

$$J = 2.2793 \times 10^{-13} \text{ g-at/cm}^2\text{-s} ,$$

$$J_{\theta L} = 5.6213 \times 10^{-13} \text{ g-at/cm-s} ,$$

$$J_{\Omega} = 1.3676 \times 10^{-12} \text{ g-at/s} ,$$

which do account for temperature dependence of the mass diffusivity, but still ignore thermal diffusion.

Equation (48) of the main body of the report combined, respectively, with Eqs. (47), (53), and (58) and the approximate equations for $E_1(z)$ lead to

$$J = 1.4964 \times 10^{-13} \text{ g-at/cm}^2\text{-s} ,$$

$$J_{\theta L} = 3.6905 \times 10^{-13} \text{ g-at/cm-s} ,$$

$$J_{\Omega} = 8.9783 \times 10^{-13} \text{ g-at/s} .$$

These results include the effects of thermal diffusion with heat of transport constant at - 10 000 g-cal/g-at, as well as variation of mass diffusivity with temperature.

Equations (66) and (64) of the main body of the report can be combined with Eqs. (65), (71), and (76) to obtain the respective results:

$$J = 1.4646 \times 10^{-13} \text{ g-at/cm}^2\text{-s} ,$$

$$J_{\theta L} = 3.6120 \times 10^{-13} \text{ g-at/cm-s} ,$$

$$J_{\Omega} = 8.7873 \times 10^{-13} \text{ g-at/cm}^2\text{-s} .$$

These values correspond to thermal diffusion with heat of transport linearly dependent upon temperature (constant term, - 21 000 g-cal/g-at; temperature coefficient, 11 g-cal/g-at.K; heat of transport, - 10 000 g-cal/g-mol at 1000 K) and temperature dependence of mass diffusivity taken into consideration.

In these numerical examples, the use of a value for mass diffusivity computed for the arithmetic mean of the barrier face temperatures has resulted in an error of the order of 10% in comparison with the flux values estimated with the analysis that considers temperature dependence of mass diffusivity. Neglect of thermal diffusion resulted in a much greater error, of the order of 60%.

APPENDIX D

ANALYSIS WHEN TEMPERATURE DEPENDENCE OF HEAT OF TRANSPORT IS STRONGER THAN LINEAR

The case:

$$Q^* = \alpha + \beta T + \delta T^2$$

for a cylindrical shell barrier will be examined as an illustrative example of the problems faced when dependences of heats of transport on temperature stronger than linear must be dealt with. The differential formulation of the problem is

$$J_{\theta L} = - D_0 e^{-\frac{Q_0}{RT}} r \left[\frac{dC}{dr} + \left(\frac{\alpha}{RT^2} + \frac{\beta}{RT} + \frac{\gamma}{R} \right) \left(\frac{dT}{dr} \right) C \right] = \text{constant}.$$

From Eq. (11) of the main body of this report

$$\frac{dT}{dr} = - \frac{(T_1 - T_2)}{\ln(r_2/r_1)} \frac{1}{r},$$

and with the changes of variables

$$\frac{dC}{dr} = \frac{dC}{dT} \frac{dT}{dr}, \quad \tau = 1/T, \quad dT = - \frac{1}{\tau^2} d\tau,$$

one obtains

$$\frac{dC}{d\tau} + \left[\frac{\alpha}{R} + \frac{\beta}{R\tau} + \frac{\gamma}{R\tau^2} \right] C = \frac{\ln(r_1/r_2)}{(T_1 - T_2)} \frac{J_{0L}}{D_0} e^{\frac{Q_D}{R} \tau}.$$

A single integration gives

$$\begin{aligned} e^{-\frac{\alpha}{R}\tau + \frac{\gamma}{R\tau}} \frac{C}{\tau^{\frac{\beta}{R}}} &= e^{-\frac{\alpha}{R}\tau_1 + \frac{\gamma}{R\tau_1}} \frac{C}{\tau_1^{\frac{\beta}{R}}} - \frac{\ln(r_2/r_1)}{(T_1 - T_2)} \frac{J_{0L}}{D_0} \int_{\tau_1}^{\tau} e^{\frac{Q_D - \alpha}{R}\tau + \frac{\gamma}{R\tau}} \frac{d\tau}{\tau^{\frac{\beta}{R}}} \\ &= e^{-\frac{\alpha}{R}\tau_1 + \frac{\gamma}{R\tau_1}} \frac{C}{\tau_1^{\frac{\beta}{R}}} - \frac{\ln(r_2/r_1)}{(T_1 - T_2)} \frac{J_{0L}}{D_0} \int_{\tau_1}^{\tau} \left[\sum_{n=0}^{\infty} \frac{\left(\frac{Q_D - \alpha}{R} \tau^2 + \frac{\gamma}{R} \right)^n}{n! \tau^{n+\beta/R}} \right] d\tau \\ &= e^{-\frac{\alpha}{R}\tau_1 + \frac{\gamma}{R\tau_1}} \frac{C}{\tau_1^{\frac{\beta}{R}}} - \frac{\ln(r_1/r_2)}{(T_1 - T_2)} \frac{J_{0L}}{D_0} \int_{\tau_1}^{\tau_2} \left[\sum_{n=0}^{\infty} \sum_{j=0}^n \frac{\left(\frac{Q_D - \alpha}{R} \right)^j \left(\frac{\gamma}{R} \right)^{n-j} \tau^{2j-n-(\beta/R)}}{j!(n-j)!} \right] d\tau \end{aligned}$$

Apparently, unless a suitable approximate expression can be found for the integrand, one has to deal with an infinite series, with each term a finite series whose length increases with term number, or with numerical quadrature.

NOMENCLATURE

a	area, $[L^2]$
A	area, $[L^2]$
C	dissolved hydrogen isotope atom concentration, $[ML^{-3}]$
C _D	diffusing hydrogen isotope atom concentration, $[ML^{-3}]$
C _H	dissolved protium atom concentration, $[ML^{-3}]$
C _{S_i}	concentration of hydrogen isotope trapping site of Type i, i = 1, . . . , I, $[ML^{-3}]$
C ₁	dissolved hydrogen isotope atom concentration at inside barrier face, $[ML^{-3}]$
C ₂	dissolved hydrogen isotope atom concentration at outside barrier face, $[ML^{-3}]$
E _{1(z)}	standard integral, Eq. (21), dimensionless
f _{H₂(g)}	fugacity in gas phase, protium diatomic molecules, $[ML^{-1}\theta^{-2}]$
f _{H(s)}	fugacity, dissolved protium atoms, $[ML^{-1}\theta^{-2}]$
f _{D(s)}	fugacity, dissolved deuterium atoms, $[ML^{-1}\theta^{-2}]$
f _{T(s)}	fugacity, dissolved tritium atoms, $[ML^{-1}\theta^{-2}]$
f ^o _{H(s)}	standard-state fugacity, dissolved protium atoms, $[ML^{-1}\theta^{-2}]$
f ^o _{D(s)}	standard-state fugacity, dissolved deuterium atoms, $[ML^{-1}\theta^{-2}]$
f ^o _{T(s)}	standard-state fugacity, dissolved tritium atoms, $[ML^{-1}\theta^{-2}]$
f _i	fraction of hydrogen isotope trapping sites of Type i which are occupied by trapped hydrogen isotope atoms, i = 1, . . . , I, dimensionless
F ₁	factor, Eq. (26), $[T^{-1}]$
F ₂	factor, Eq. (48), $[T^{-1}]$
F ₃	factor, Eq. (66), $[T^{-1}]$
$\bar{g}_{H(s)}^o$	partial molal Gibbs free energy of dissolved protium atoms in standard state, $[L^2\theta^{-2}]$

ΔG_H°	standard molar Gibbs free-energy change for dissolution of protium in metal, $[L^2\theta^{-2}]$
i	type of hydrogen isotope atom trapping site, dimensionless
I	number of types of hydrogen isotope atom trapping sites, dimensionless
ΔH_H°	standard molar heat of solution for dissolution of protium in metal, $[L^2\theta^{-2}]$
j	term number, dimensionless
J	diffusion flux, $[ML^{-2}\theta^{-1}]$
$\vec{J}$	vectorial diffusion flux, $[ML^{-2}\theta^{-1}]$
$J_{\theta L}$	diffusion flux, cylindrical shell, $[ML^{-1}\theta^{-1}]$
J_{Ω}	diffusion flux, spherical shell, $[M\theta^{-1}]$
k	thermal conductivity of metal, $[ML\theta^{-3}T^{-1}]$
$k_{1,i}$	rate constant for trapping of hydrogen isotope atoms by sites of Type i , $i = 1, \dots, I$, $[\theta^{-1}]$
$k_{2,i}$	rate constant for release of trapped hydrogen isotope atoms by sites of Type i , $i = 1, \dots, I$, $[M^{-n_i}L^{3n_i}\theta]$
K_H	solubility constant, protium atoms in metal, $[M^{-1}L\theta^2]$
K_D	solubility constant, deuterium atoms in metal, $[M^{-1}L\theta^2]$
K_T	solubility constant, tritium atoms in metal, $[M^{-1}L\theta^2]$
K_{EQ_H}	equilibrium constant, protium diatomic molecule dissolution in metal, dimensionless
$K_{EQ_H}^\circ$	preexponential factor, equilibrium constant, protium diatomic molecule dissolution in metal, dimensionless
K_{H_2}	dissociation constant, protium diatomic molecules, $[ML^{-1}\theta^{-2}]$
K_{D_2}	dissociation constant, deuterium diatomic molecules, $[ML^{-1}\theta^{-2}]$
K_{T_2}	dissociation constant, tritium diatomic molecules, $[ML^{-1}\theta^{-2}]$
K_{HD}	equilibrium constant, equilibrium between H_2 , D_2 , and HD , dimensionless

K_{HT}	equilibrium constant, equilibrium between H_2 , T_2 , and HT , dimensionless
K_{DT}	equilibrium constant, equilibrium between D_2 , T_2 , and DT , dimensionless
K_{S_H}	Sieverts' law constant, protium $[M^{-1/2}L^{1/2}\theta]$
K_{S_D}	Sieverts' law constant, deuterium, $[M^{-1/2}L^{1/2}\theta]$
K_{S_T}	Sieverts' law constant, tritium, $[M^{-1/2}L^{1/2}\theta]$
$K_{S_{Total}}$	Sieverts' law constant, hydrogen isotope mixture, $[M^{-1/2}L^{1/2}\theta]$
K_S°	preexponential factor, Sieverts' law, $[M^{-1/2}L^{1/2}\theta]$
$K_{S_H}^\circ$	preexponential factor, Sieverts' law, protium, $[M^{-1/2}L^{1/2}\theta]$
$K_{S_D}^\circ$	preexponential factor, Sieverts' law, deuterium, $[M^{-1/2}L^{1/2}\theta]$
$K_{S_T}^\circ$	preexponential factor, Sieverts' law, tritium, $[M^{-1/2}L^{1/2}\theta]$
K_{Total}	solubility constant, hydrogen isotope mixture, atomic basis, $[M^{-1}L\theta^2]$
ℓ	distance along cylindrical shell, $[L]$
L	cylindrical shell length, $[L]$
m	specific absorption, $[ML^{-2}]$
$m_{\theta L}$	specific absorption, pipe wall, $[ML^{-1}]$
m_Ω	specific absorption, spherical shell, $[M]$
M_M	molecular weight of metal, dimensionless
n	term number, dimensionless
n_i	number of dissolved hydrogen atoms trapped by each site of Type i , $i = 1, \dots, I$, dimensionless
N	atom ratio, dissolved hydrogen isotope atoms to metal atoms, dimensionless
$N_{H(s)}$	atom ratio, protium dissolved in metal, dimensionless
$N_{D(s)}$	atom ratio, deuterium dissolved in metal, dimensionless
$N_{T(s)}$	atom ratio, tritium dissolved in metal, dimensionless

N_{Total}	atom ratio, gross for mixture of hydrogen isotope atoms dissolved in metal, dimensionless
p	pressure, $[\text{ML}^{-1}\theta^{-2}]$
p_{HD}	partial pressure, HD, $[\text{ML}^{-1}\theta^{-2}]$
p_{H_2}	partial pressure, protium molecules in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_{H}	partial pressure, protium atoms in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_{D_2}	partial pressure, deuterium molecules in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_{D}	partial pressure, deuterium atoms in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_{T_2}	partial pressure, tritium molecules in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_{T}	partial pressure, tritium atoms in gas phase, $[\text{ML}^{-1}\theta^{-2}]$
p_1	gas-phase pressure of hydrogen isotope molecules at inner barrier face, $[\text{ML}^{-1}\theta^{-2}]$
p_2	gas-phase pressure of hydrogen isotope molecules at outer barrier face, $[\text{ML}^{-1}\theta^{-2}]$
q	heat flux, $[\text{M}\theta^{-3}]$
q^*	heat flux, $[\text{ML}^2\theta^{-3}]$
Q_{D}	activation energy for diffusion of hydrogen isotope atoms in metal, $[\text{L}^2\theta^{-2}]$
Q_{P}	activation energy for permeation of hydrogen isotope atoms through metal barrier, $[\text{L}^2\theta^{-2}]$
Q_{S}	heat of solution for hydrogen isotopes, Sieverts' law, $[\text{L}^2\theta^{-2}]$
Q_{S_H}	heat of solution, protium, Sieverts' law $[\text{L}^2\theta^{-2}]$
Q_{S_D}	heat of solution, deuterium, Sieverts' law $[\text{L}^2\theta^{-2}]$
Q_{S_T}	heat of solution, tritium, Sieverts' law $[\text{L}^2\theta^{-2}]$
Q^*	heat of transport for hydrogen isotope atoms in metal, $[\text{L}^2\theta^{-2}]$
r	radial coordinate, $[\text{L}]$
r_1	inside radius of cylindrical or spherical shell, $[\text{L}]$

r_2	outside radius of cylindrical or spherical shell, [L]
R	ideal gas constant, [$L^2\theta^{-2}T^{-1}$]
S	surface area of arbitrary volume, [L^2]
$\vec{S}$	outwardly directed surface-area vector, [L^2]
ΔS_H°	standard molar entropy change upon dissolution of protium in metal, [$L^2\theta^{-2}T^{-1}$]
t	time, [θ]
T	absolute temperature, [T]
T_1	absolute temperature at inner barrier face, [T]
T_2	absolute temperature at outer barrier face, [T]
u	dummy variable, Eq. (21), dimensionless
V	arbitrary volume, [L^3]
$x_{H(s)}$	mole fraction of protium atoms dissolved metal, dimensionless
x	position coordinate through plane barrier, [L]
x_1	position of inside face of plane barrier, [L]
x_2	position of outside face of plane barrier, [L]
y_{H_2}	mole fraction of protium diatomic molecules in gas phase, dimensionless
y_{D_2}	mole fraction of deuterium molecules in gas phase, dimensionless
y_{T_2}	mole fraction of tritium diatomic molecules in gas phase, dimensionless
y_{HD}	mole fraction of HD in gas phase, dimensionless
$y_{H_2}^\circ$	mole fraction of protium diatomic molecules in gas phase before isotope exchange, dimensionless
$y_{D_2}^\circ$	mole fraction of deuterium diatomic molecules in gas phase before isotope exchange, dimensionless
$y_{T_2}^\circ$	mole fraction of tritium diatomic molecules in gas phase before isotope exchange, dimensionless
z	dummy variable, Eq. (21), dimensionless

Greek Letters

α	constant term in linear expression for heat of transport as a function of temperature, $[L^2\theta^{-2}]$
β	temperature coefficient in linear expression for heat of transport as a function of temperature, $[L^2\theta^{-2}T^{-1}]$
$\gamma_{H(s)}$	activity coefficient for protium atoms dissolved in metal, dimensionless
δ	coefficient of temperature to the second power in quadratic expression for heat of transport, $[L^2\theta^{-2}T^{-2}]$
ϵ	error, dimensionless
ζ	function of τ , Eq. (23), $[T]$
η	function of τ , Eq. (23), $[T]$
θ	cylindrical shell angle, Fig. 1b, dimensionless
λ	dummy parameter, Eq. (23), $[T]$
μ	function of τ , Eq. (64), $[T^{\beta/R+1}]$
ρ_m	density of metal, $[ML^{-3}]$
σ	Euler's constant, dimensionless
τ	reciprocal temperature, $[T^{-1}]$
τ_1	reciprocal temperature at inner barrier face, $[T^{-1}]$
τ_2	reciprocal temperature at outer barrier face, $[T^{-1}]$
ϕ	constant term in linear expression for thermal conductivity as a function of temperature, $[ML^{-3}T^{-1}]$
ψ	temperature coefficient in linear expression for thermal conductivity as a function of temperature, $[ML^{-3}T^{-2}]$
ω	spherical-shell solid angle, dimensionless
Ω	spherical-shell solid angle, Fig. 1c, dimensionless

Special Symbols

D	mass diffusivity, $[L^2\theta^{-1}]$
D_0	preexponential factor in Arrhenius expression for mass diffusivity of hydrogen isotope atoms in metal, $[L^2\theta^{-1}]$
J	total transfer rate for hydrogen isotope atoms through barrier, $[M\theta^{-1}]$
M	total absorption of hydrogen isotope atoms by barrier, $[M]$
P	permeability for hydrogen isotope atoms through barrier, $[M^{1/2}L^{-1/2}]$
P_0	preexponential factor, Arrhenius expression for permeability of hydrogen isotope atoms through barrier, $[M^{1/2}L^{-1/2}]$
R	resistance to transfer of hydrogen isotope atoms through barrier, $[L^{-1}\theta]$
$R_{\theta L}$	resistance to transfer of hydrogen isotope atoms through cylindrical shell, $[L^{-2}\theta]$
R_{Ω}	resistance to transfer of hydrogen isotope atoms through spherical shell, $[L^{-3}\theta]$

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