Review

Isotope effect of hydrogen and deuterium permeability and diffusivity in fusion reactor materials. A literature review

María Urrestizala [*], Jon Azkurreta , Natalia Alegría , Igor Peñalva

Department of Energy Engineering, University of the Basque Country (UPV/EHU), Ingeniero Torres Quevedo Plaza, 1, Bilbao, Biscay 48013, Spain

A B S T R A C T

The characterization of hydrogen transport parameters is essential for a good prediction of its behavior and a correct design of the elements that will make up nuclear fusion reactors. It is therefore essential to determine the isotopic ratio of the transport parameters between protium (H), deuterium (D) and tritium (T), both for economic and safety reasons. Classical theory predicts that the ratio of their diffusivities and permeabilities should be proportional to the inverse square root of their atomic mass, while solubility values would be independent of their masses, but there are discrepancies in the literature. Despite this, it has not yet been possible to obtain either a correct value for the ratio or any uniform conclusion on the matter. This article presents a review of the works published in the field of the isotope effect of hydrogen permeability and diffusivity to date, focusing on protium and deuterium isotopes, which are the isotopes that have been most extensively analyzed experimentally. The conclusion is clear: the theoretical value cannot be stated to be correct and the results are very varied, although they seem to be related to the microstructure of the material tested. In addition, some factors that could have an influence on it have been analyzed, which would be interesting to take into account for future studies.

1. Introduction

Nuclear fusion is the main technology capable of producing clean energy on a massive scale and requires processes in which its elements must work at high temperatures under the influence of hydrogen isotopes (protium (H), deuterium (D) and tritium (T)), as these will constitute the fuel required for this energy source. Therefore, among the many technological challenges facing its development, the transport of isotopes through different metals and their interaction represents one of the main problems, especially at elevated temperatures, since their behavior exhibits an Arrhenius dependence on temperature. Consequently, the interaction of metals and hydrogen isotopes represents one of the main lines of research in this area.

In fact, the transport of hydrogen isotopes through the different materials that constitute a fusion reactor determines its operation for several reasons. In addition to the constraints relating to the necessary radiological protection that must be ensured for the operators of the reactor, the net balance of the transport of these isotopes through the materials affects the fuel cycle operating in a closed loop, so it is a key issue in the design of the reactor elements themselves. Moreover, protium and deuterium retention could also become a problem, as it

produces damage and structural degradation of several elements [1–3]. Finally, the permeation of tritium outwards is an additional environmental issue, as tritium is radioactive [4–7]. For all these reasons, characterization of the behavior of hydrogen isotopes in contact with the different materials that will compose the fusion reactors, is essential to quantify the main reactor design constraints, as well as the safety, viability, and stability of the plasma. To this end, numerous experimental studies are necessary.

It is true that hydrogen transport parameters are currently being measured experimentally in different fusion-materials of interest, such as Tungsten Alloys [8], Reduced Activation Ferritic/Martensitic Steels (RAF/M) [9], Vanadium Alloys [10],... to define permeability and diffusivity in diffusive regimes. However, carrying out this large number of experimental measurements with deuterium and tritium is not very feasible and makes progress in this line of research somewhat slow. The difficulty with deuterium is that it is found in nature with an abundance of 0.015 % of hydrogen atoms (one in 6500) [11]. In the case of tritium, the difficulty is that it is a radioactive isotope, as mentioned above. Therefore, a correct description of the relationship between the isotope parameters (the so-called isotope effect) is urgently needed, so that the deuterium-material and, especially, tritium-material interaction can be

extrapolated from the properties of protium, which is an abundant, safe and feasible isotope for experimental research. In this way, research on the interaction of hydrogen isotopes with different reactor materials will be firmly advanced and, consequently, further progress will be made in the development of fusion.

2. Justification

As mentioned above, in the area of nuclear fusion research, it would be very useful if the characterization experiments of the hydrogen transport parameters could always be carried out only with protium and, from the values obtained, the parameters of the other two isotopes (deuterium and tritium) could be obtained.

For many years, this relationship was thought to be in accordance with classical atomic theory (see Eq. (1)), which relates diffusivity to atomic vibrational frequencies and establishes these frequencies as inversely proportional to masses [12].

$$D_\alpha/D_\beta = \sqrt{m_\beta/m_\alpha} \qquad (1)$$

Where m^β and m^α mean mass of isotope β and α, respectively, as hydrogen atoms can be regarded as classical particles at high temperatures, which hop over the potential barrier via thermal excitation [13].

Therefore, the respective permeability rates should have the same relationship [14] (Eq. (2)), whereas those for solubility should be independent of the masses of the hydrogen isotopes [15].

$$\Phi_\alpha/\Phi_\beta = \sqrt{m_\beta/m_\alpha} \qquad (2)$$

According to these equations, the diffusion and permeability coefficients are inversely proportional to the square root of the mass ratio, and the activation energies should be independent of the mass ratio.

However, some discrepancies have been detected in the literature, and the isotopic ratio described is not always supported; thus, the need to study this relationship is reaffirmed. A precise, specific, and accurate description of the isotope effects on hydrogen transport is urgently needed. An adjusted isotopic description will allow, on the one hand, to differentiate the behavior of deuterium and tritium within the covering structures under future reactor operating conditions and studying the tritium regeneration process in advance [16]. But above all, in this way, deuterium-material and, especially, tritium-material interaction may be extrapolated correctly. Consequently, the investigation of tritium effects and transport will become technologically more feasible, as it will not be necessary to work with a radioactive isotope when performing the various experiments. This will be a great advantage, since the measurement of tritium permeability and diffusivity with pure gas often poses a challenge, on the one hand, of safety, associated with handling a large amount of it; on the other hand, because of its low abundance. Consequently, the available data about experimental studies with it are far inferior to those of the other two isotopes [17,18], and the facilities available for its experimentation, a very small minority, highly complex and therefore with a large financial backing [19–22]. Therefore, the possibility of working with a correct extrapolation would be a good step forward.

In this context, and due to the discrepancies and lack of agreement between the analyses performed for the isotope effect and the directions they take, the present work is considered to be of great necessity. The aim is to make a bibliographic compilation of the studies carried out to date that have published the Arrhenius equations of diffusivity and/or permeability for both protium and deuterium, in order to obtain from these the different experimental isotope ratios for different materials and processes. This will provide a common record of the values obtained and make it easier to deduce whether there is any common trend among the studies carried out.

3. Theory and calculations

This section summarises the basic theory and equations for understanding the behavior of hydrogen in contact with materials in a predominantly diffusive regime.

Typical parameters for the study of hydrogen transport within metal lattices are diffusivity (D), Sieverts constant (K_S) and permeability (Φ) [23].

The diffusivity is defined by the following Arrhenius-type expression (Eq. (3)):

$$D = D_0 \exp(-E_d/RT) \qquad (3)$$

where D_0 is the pre-exponential diffusion factor, also called frequency factor, R is the ideal gas constant and E_d is the activation energy of diffusion.

The proportionality between the atomic gas concentration (c) within the volume and the square root of the equilibrium pressure (p) of the gas outside the material is known as the Sieverts constant (Eq. (4)):

$$K_S = c/\sqrt{p} \qquad (4)$$

Interestingly, the Sieverts constant also shows an Arrhenius-like trend with temperature (Eq. (5)):

$$K_S = K_{S,0} \exp(-E_s/RT) \qquad (5)$$

Where $K_{S,0}$ is the pre-exponential factor or frequency factor of the constant and E_s is the activation energy of solution, which can be positive or negative depending on the thermodynamic characteristics of the solution in the crystal lattice.

Permeability (Φ) is defined by Richardson's law as the product of diffusivity and Sieverts constant [23] (Eq. (6)):

$$\Phi = K_s \, D \qquad (6)$$

It is clear, therefore, that the permeability also follows an Arrhenius-type relationship, with a permeation activation energy, E_Φ, resulting from E_d and E_s (Eq. (7))

$$\Phi = \Phi_0 \exp(-E_\Phi/RT) = (K_{S,0} \, D_0)\exp(-(E_s + E_d)/RT) \qquad (7)$$

For the present literature review, many studies for different materials carried out by different authors have been compiled, in which the Arrhenius equation for diffusivity and permeability has been published.

In this way, if their corresponding Arrhenius equations are related, as indicated by the expressions 8 and 9, their isotopic ratio is achieved.

$$\frac{D_H}{D_D} = \frac{D_{0\,H}\exp(-E_{d\,H}/RT)}{D_{0\,D}\exp(-E_{d\,D}/RT)} = \frac{D_{0\,H}}{D_{0\,D}}\exp(-(E_{d\,H} - E_{d\,D})/RT) \qquad (8)$$

$$\frac{\Phi_H}{\Phi_D} = \frac{\Phi_{0\,H}\exp(-E_{\Phi\,H}/RT)}{\Phi_{0\,D}\exp(-E_{\Phi\,D}/RT)} = \frac{\Phi_{0\,H}}{\Phi_{0\,D}}\exp(-(E_{\Phi\,H} - E_{\Phi\,D})/RT) \qquad (9)$$

These expressions will determine the isotope effect obtained in each case. By representing them for the temperatures at which they have been derived, it can be seen how far or close they are to the classical value.

For a correct analysis of the isotope effect, it is believed necessary that the same author performs the different tests using exactly the same material, installation and conditions, as it would not make sense to mix the results obtained under different circumstances, as the resulting isotope effect would not be really adjusted and could be distorted by some other factor.

Therefore, the indispensable condition for compiling the papers in this review have been the following: the authors have published the expressions for the diffusivity (Eq. (3)) and permeability (Eq. (7)) of hydrogen and deuterium under exactly the same circumstances following the same models, same equipment, same material samples (materials of interest for fusion reactors), same temperature ranges and pressure ranges.

Once equations for both deuterium and protium have been obtained,

dividing them, the Eqs. (8) and (9) have been derived.

Due to its scientific and industrial importance, much attention has been paid to the permeability of hydrogen through various materials for many years. While most of these analyses have studied the behavior of protium, some authors [13,24–49] have also reported the behavior of deuterium. However, in these cases, much of the data only includes permeability or diffusivity and only a few authors have reported on permeability and diffusivity, and even more rarely on both deuterium and protium. Moreover, very limited number of authors has carried out the analysis of these in more detail than a simple presentation of the data obtained. Regarding tritium, as mentioned above, and in fact as one of the main reasons behind the need to study the isotope effect, it is very difficult to find complete published data on it, and even more difficult to find it together with the other two isotopes.

Therefore, the available literature for the present analysis is somewhat difficult to obtain, despite its large interest and the fact that the analyses can easily be found separately for a single isotope (protium or deuterium) or for different conditions.

4. Results

Tables 1 and 2 below show the permeability and diffusivity isotope ratios obtained from the literature, as explained in the calculation section. The temperature range for which the work was carried out, the method used to obtain them and, of course, the material used are also included.

Similarly, these equations have been plotted on the two graphs, Figs. 1 and 2.

As can be seen, the results are varied, both in the pre-exponential factor and in the activation energies, sometimes being close to the value predicted by the theory $(\sqrt{2})$ and sometimes quite far off. Regarding the absolute value, it is interesting to note how most of the permeability curves are above the classical value over most of the temperature range represented and the opposite happens in the case of diffusivity. In this second case, there are even situations in which we find isotope ratios close to becoming inverse, in which deuterium would have a faster diffusivity than protium, reaching D_H/D_D values lower than unity. It can be observed in the case of the nickel tests, especially that of Noh (2014) [41]. Therefore, they provide a clear example of why it would be totally incorrect to apply classical theory directly. Following the real logic in these cases, and especially at lower temperatures, the tritium diffusivity would be even higher and not the opposite, as would be expected. Admittedly, the inverse relation also occurs on one occasion in the case of permeabilities. However, in this case, no generic conclusions may be drawn, since it is a very isolated case of stainless steel [33], whereas the rest of the results with similar materials are in a range above the theoretical ratio by far.

Apart from that, as far as the variation of each curve is concerned, there is a further contradiction to the classical theory: equations with a strong temperature dependence can be found, which are easily observable due to their pronounced slope, as in the case of the permeability of the steels [13,51,39,50,48] or the diffusivities of V [24] or W [53,

Table 1
Isotope ratios for permeability from published works.

ISOTOPE RATIO [-]	MATERIAL	REF	T [K]	METHOD
$\Phi_H/\Phi_D=1.17\exp(1.4\times10^3/RT)$	316 SS	(T. Shiraishi, 1999, 316 SS) [25]	473–973	Co-current double tube method
$\Phi_H/\Phi_D=1.15\exp(2.3\times10^3/RT)$	316 L SS	(S.K. Lee, 2014, 316 L SS) [13]	623–1123	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.28\exp(0.9\times10^3/RT)$	316LN SS	(W.J. Byeon, 2020, 316LN SS) [35]	573–1123	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.57\exp(1.01\times10^3/RT)$	304 SS	(H. Katsuta, 1981, 304 SS) [32]	812–1190	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.14\exp(-0.7\times10^3/RT)$	310 SS	[33] (N. R. Quick, 1979, 310 SS)	427–779	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=3.62\exp(-3.5\times10^3/RT)$	EOROFER97 (RAM)	[50](A. Aiello, 2002, EUROFER97)	473–723	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.2\exp(0.7\times10^3/RT)$	RAFM 8% CrWVTa steel	(G. A. Esteban, 2001, RAFM)[34]	423–892	Isovolumetric desorption
$\Phi_H/\Phi_D=1.18\exp(1.7\times10^3/RT)$	Ti-RAFM	(W.J. Byeon, 2020, Ti-RAFM) [36]	433–873	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=0.983\exp(2.7\times10^3/RT)$	ARAA (RAFM)	(S. J. Noh, 2014, RAFM)([51]	523–873	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.26\exp(1.37\times10^3/RT)$	F82H RAM	(E. Serra, 1998, RAM) [37,38]	373–743	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.08\exp(3\times10^3/RT)$	F82H steel	(T.V. Kulsartov, 2006, F82H steel)[39]	473–873	Diffusion cell. Permanent outlet chamber pumping-out.
$\Phi_H/\Phi_D=1.66$	sputter-deposited W coated F82F (SP-W)	(Y. Xu, 2017, SP-W-F82H) [47]	473–823	Gas Driven Permeation test
$\Phi_H/\Phi_D=1.12\exp(0.26\times10^3/RT)$	Fe	(N.R. Quick, 1978, Fe)[40]	323–779	Permeation test
$\Phi_H/\Phi_D=1.28\exp(1.3\times10^3/RT)$	Ni	(S. J. Noh, 2014, Ni) [41]	723–1123	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.17\exp(1.4\times10^3/RT)$	Ni	(T. Shiraishi,1998, Ni) [42]	473–973	Co-current double tube method
$\Phi_H/\Phi_D=1.36\exp(1.0\times10^3/RT)$	Ni	(W. Eichenauer, 1965, Ni) [43]	663–933	Isovolumetric desorption
$\Phi_H/\Phi_D=1.63\exp(-0.5\times10^3/RT)$	Ni	(Y. Ebisuzaki, 1967, Ni) [26]	473–693	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.35\exp(1.0\times10^3/RT)$	ELBRODUR G CuCrZr	(S.J. Noh, 2016, ELBRODUR G CuCrZr) [44]	573–873	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=1.54\exp(-0.15\times10^3/RT)$	Pd-Ag	(E. Serra, 1998, Pd-Ag) [45]	323–773	Permeation test. Continuous Gas Phase Method
$\Phi_H/\Phi_D=2.05\exp(-1.14\times10^3/RT)$	Pd-Ag	(M. Nishikawa, 1996, Pd-Ag) [46]	353–673	Co-current double tube method
$\Phi_H/\Phi_D=1.09\exp(2.5\times10^3/RT)$	W	(G. A. Esteban, 2001, W) [48]	673–1073	Isovolumetric desorption

Table 2
Isotope ratios for diffusivity from published works.

ISOTOPE RATIO [-]	MATERIAL	REF	T° [K]	Method
$D_H/D_D = 1.51\exp(1.85 \times 10^3/RT)$	304 SS	(H. Katsuta, 1981, 304 SS) [32]	812–1190	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.61\exp(0.72 \times 10^3/RT)$	310 SS	(N. R. Quick, 1979, 310 SS) [33]	427–779	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 0.9\exp(2.4 \times 10^3/RT)$	316 L SS	(S.K. Lee, 2014, 316 L SS) [13]	623–1123	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.15\exp(0.3 \times 10^3/RT)$	316LN SS	(W.J. Byeon, 2020, 316LN SS) [35]	433–873	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.19\exp(0.75 \times 10^3/RT)$	RAFM 8% CrWVTa steel	(G. A. Esteban, 2001, RAFM) [34]	423–892	Single isovolumetric desorption
$D_H/D_D = 1.02\exp(1.1 \times 10^3/RT)$	Ti-RAFM	(W.J. Byeon, 2020, Ti-RAFM) [36]	433–873	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.68\exp(-0.1 \times 10^3/RT)$	F82H RAM	(E. Serra, 1998, RAM) [37,38]	373–743	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.38$	F82H RAFM	(Y. Xu, 2017, RAFM) [49]	423–773	Gas Driven Permeation test
$D_H/D_D = 1.22\exp(-0.2 \times 10^3/RT)$	F82H steel	(T.V. Kulsartov, 2005, F82H steel) [39]	473–873	Diffusion cell. Permanent outlet chamber pumping-out.
$D_H/D_D = 1.54$	SP- W coated F82H	(Y. Xu, 2017, SP-W-F82H) [47]	473–823	Gas Driven Permeation test
$D_H/D_D = 1.06\exp(0.24 \times 10^3/RT)$	Fe	(N.R. Quick, 1978, Fe) [40]	323–779	Permeation test
$D_H/D_D = 1.42\exp(-1.2 \times 10^3/RT)$	Ni	(S. J. Noh, 2014, Ni) [41]	473–973	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.40\exp(-1.1 \times 10^{-3}/RT)$	Ni	(W. Eichenauer, 1965, Ni) [43]	663–933	Isovolumetric desorption
$D_H/D_D = 1.31\exp(-0.7 \times 10^3/RT)$	Ni	(Y. Ebisuzaki, 1967, Ni) [26]	473–693	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.34\exp(-0.19 \times 10^3/RT)$	Ni	[27](L. Katz, 1970, Ni)	673–1273	Isovolumetric desorption
$D_H/D_D = 1.3\exp(-0.8 \times 10^3/RT)$	Ni	(Y. Hayashi, 1985, Ni) [52]	523–974	Permeation test
$D_H/D_D = 1.78\exp(-0.6 \times 10^3/RT)$	ELBRODUR G CuCrZr	(S.J. Noh, 2016, ELBRODUR G CuCrZr) [44]	573–873	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 1.64\exp(-1.22 \times 10^3/RT)$	Pd-Ag	(E. Serra, 1998, Pd-Ag) [45]	323–773	Permeation test. Continuous Gas Phase Method
$D_H/D_D = 2.12\exp(-2.3 \times 10^3/RT)$	Pd-Ag	(M. Nishikawa, 1996, Pd-Ag) [46]	353–673	Co-current double tube method
$D_H/D_D = 0.96\exp(2.3 \times 10^3/RT)$	Nb	(G. Völkl, 1978, Nb) [24]	Aprox 123–1000	–
$D_H/D_D = 0.90\exp(2.3 \times 10^3/RT)$	Ta	(G. Völkl, 1978, Ta) [24]	Aprox 350–673	–
$D_H/D_D = 0.8\exp(3.7 \times 10^3/RT)$	V	(G. Völkl, 1978, V) [24]	Aprox 123–773	–
$D_H/D_D = 1.04\exp(0.7 \times 10^3/RT)$	W	(G. A. Esteban, 2001, W) [48]	673–1073	Isovolumetric desorption
$D_H/D_D = 0.534\exp(11.4 \times 10^3/RT)$	W	(H. Nakamura, 2001, W) [53]	525–715	Permeation test

whose values are well outside the limits of the graph and therefore cannot even be observed (Nakamura's line takes values between 3.5 and 7.5 in the temperature range tested). It is important to note that, in these cases, the inappropriate use of temperatures or approximations could lead to larger errors in the quantification of the isotope effect, as the isotope effect is supposed to be independent of temperature and in these cases its dependence is very high. Therefore, extrapolations to other isotopes in these cases could lead to larger errors due to their high dependence. On the other hand, there are cases that have a high isotopic dependence (high absolute value), but their sensitivity to temperature is negligible, and the curve remains fairly horizontal in the represented range. This phenomenon occurs, for example, in SP-W-F82H [47] permeability and diffusivity or RAM [37,38] diffusivity. Similar cases of horizontality and thus independence with temperature can also be found, but with less isotopic dependence than the classical one, as is the case for diffusivity of steel [39] or Ni [27].

In the case of permeability, as mentioned, most of the curves are above the theoretical value and tend to be closer to it at very high temperatures in almost all cases, excluding Fe [40], Pd-Ag [45,46], one case of Ni [26] and steels [33,50]. It should be noted the cases of Fe [40], 310SS [33], with values well below the classical one, but very close to unity, especially in the second one mentioned, which would indicate a very low isotope effect in the tested temperature range, and therefore, very similar results for hydrogen and deuterium in these analyses.

In the case of diffusivity, quite different trends can be observed, and less general conclusions can be drawn. One group of curves, despite the fact that at lower and/or higher temperatures they deviate, is quite close to the predicted value in the range of 600 K-800 K (steels [13,34,49] Ta [24], V [24], Nb [24], Pd-Ag [45]). Another group is below this theoretical value in almost all cases, but they are very close to each other, with a value of about 1.2 (Fe [40], Ni [26,41,43,52], W [48] and some steels [35,36,39]). While a small minority are considerably above the theory, although with values quite scattered among them (most of them are steels, such as [32,33]).

It is curious how some authors claim that stainless steels usually stick to the classical value quite acceptably in the temperature range of interest for fusion technology, so that for these materials the classical formula is a fairly good predictor [4,14,54]. Furthermore, it is said that their permeability is not very sensitive to the composition of the alloys [55,56]. However, it has been observed that this is not always the case, and authors present results that differ from each other, finding significant differences between each other's expressions. Still, although the resulting values are different, it can be stated that the general trends hold, as they are made of different combinations of materials, and these alloys tend to make the trends more stable. In most cases, the D_H/D_D ratio decreases very slowly with increasing temperature for these steels and Φ_H/Φ_D ratio also decreases but in a more abrupt way.

The same happens with other metals, showing similar tendencies between them in some occasions. This phenomenon occurs more strongly in studies carried out directly with simple elements, as in the case of nickel, where it can be observed that the lines are practically overlapped in some cases, being highly coincident diffusivities of [26, 41,43,52]. Consequently, it could be said that, although the classical relationship is not fulfilled in these cases, the difference with respect to this one is coincident and therefore could be closely linked to the type of material tested.
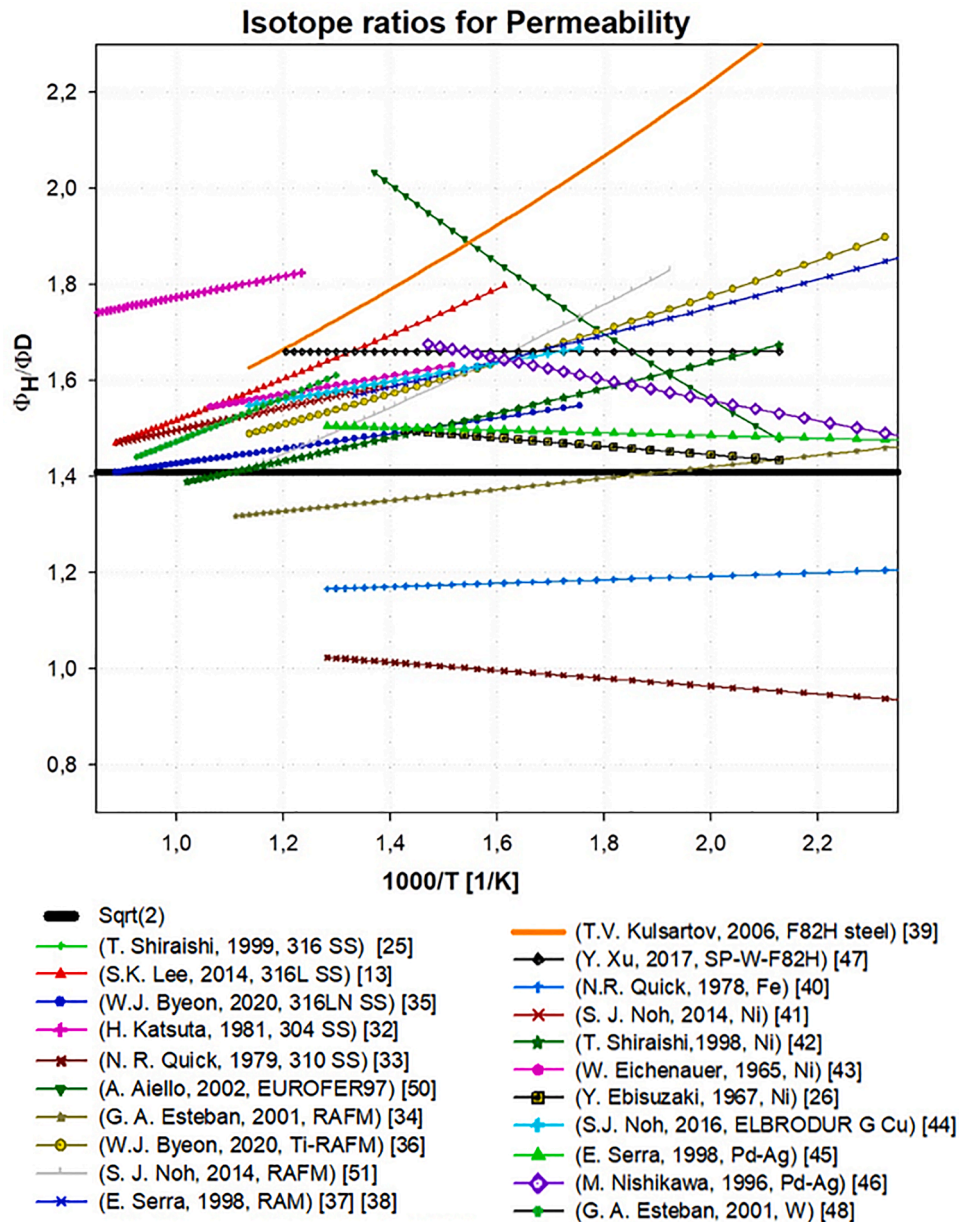
Fig. 1. Isotope Ratios for Permeability.

However, it is also true that there are studies carried out with similar materials whose results show quite different isotope effects (such as W or [32] stainless steel comparing with the others), so it is undeniable that the ratio depends on other factors as well.

5. Discussion

To begin with this section, it will be stated that the isotopic ratio of permeabilities and diffusivities between protium and deuterium does not meet the classical value, and moreover, the published values differ considerably from each other. The reasons and possible explanations and factors that may affect this analysis will be discussed below.

First of all, it is important to note that the fact that hydrogen has the highest possible isotopic mass ratio of all the elements among its various isotopes makes these effects considerable, as the effects are maximised [33,34]. Clearly, the greater the difference between the masses of the isotopes, the greater the deviations from the theories, and in the case of protium and deuterium, the latter has a mass that is two times larger.

Moreover, the fact that permeability and diffusivity show opposite

trends, (most permeability ratios are higher than $\sqrt{2}$ and most diffusivity ratios are lower) can be seen to mean that solubility would not be independent of atomic masses in this case, and would also be affected by the isotope effect, so that Eq. (6) is fulfilled. Therefore, it can be argued that this point of the classical theory would not be correct either, and an isotopic dependence would be found in all three cases, which would make the study and prediction of the values more difficult.

Regarding the activation energies, if the data collected and plotted (Figs. 1 and 2) are analyzed, the classical prediction that activation energies are mass-independent is also wrong. This is an evident conclusion that can be confirmed, since otherwise a much more horizontal trend would be found for the curves drawn. But the most remarkable point is that the difference with respect to this independence, in the case of diffusivity, does not seem to be random. The upward and downward trend of diffusivity follows a common pattern: the dependence of diffusivity on isotopic mass is clearly correlated with the microstructure of the host metal. In order to see this difference in trends more visually, the figure of diffusivity ratios (Fig. 2) has been subdivided according to materials, thus creating Figs. 3 and 4.
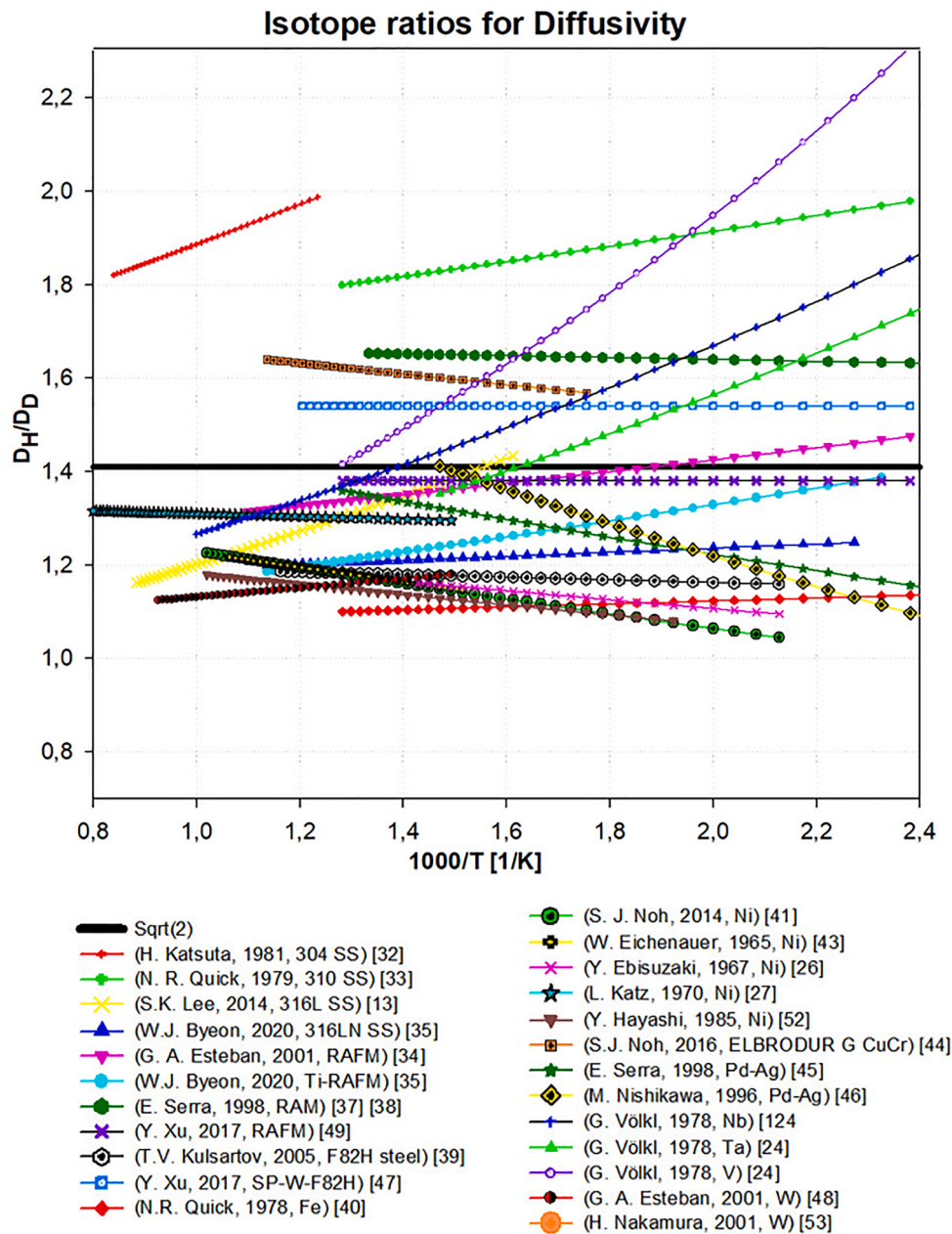
Fig. 2. Isotope Ratios for Diffusivity.

To check this, it is observed that, 100% of the tests performed with materials whose microstructure type is fcc (Pd, Ag, Ni, Cu alloys…), have a negative exponential factor in their isotope ratio equation, and therefore, resulting expressions increase with increasing temperature. The translation of this is, then, that in these cases, deuterium has a lower diffusion activation energy than protium, so the activation energies of diffusion decrease with the mass increase, and this would lead to an inverse isotope effect at low temperatures. Fig. 3 shows how in some cases of nickel, for example, deuterium would diffuse faster than hydrogen at temperatures below about 450 K if the lines shown were extrapolated [41,43] .

In the works with materials with bcc microstructure (V, Nb, Ta, W) and most of the stainless steels analyzed (although not all), on the other hand (Fig. 4), the opposite trend is found. It appears the usual isotope ratio, in which deuterium will have a higher activation energy than protium in the whole temperature regime investigated, so larger activation energies are observed for larger mass isotope. Consequently, diffusivity ratio expressions decrease with increasing temperature;

therefore, the isotope ratio curves represented in this case show an upward trend.

This conclusion is something already predicted by Völk [24]. According to several authors [57–59], the reason for this opposite behavior between the two types of materials could be the preference of the interstitial solution site in each case, since in fcc structures the H atoms will mostly occupy the octahedral interstitial sites, and in bcc structures the tetrahedral ones. The minimum distance between two interstitial sites, according to this theory, is shorter for bcc (between 1.01 and 1.17 Å), than for fcc (between 2.5 and 2.9 Å). A shorter distance can translate into a smaller activation barrier (less diffusion diffculties) and also easier tunnelling [24].

In any case, it is important to note the fully coincident behavior that, considering the experimental temperatures for which they have been tested, the higher the isotopic mass, the higher the diffusion energy in all the bcc materials included in this review.

Apart from the trends described in relation to the microstructure, it can be categorically stated, after analysing a large number of studies
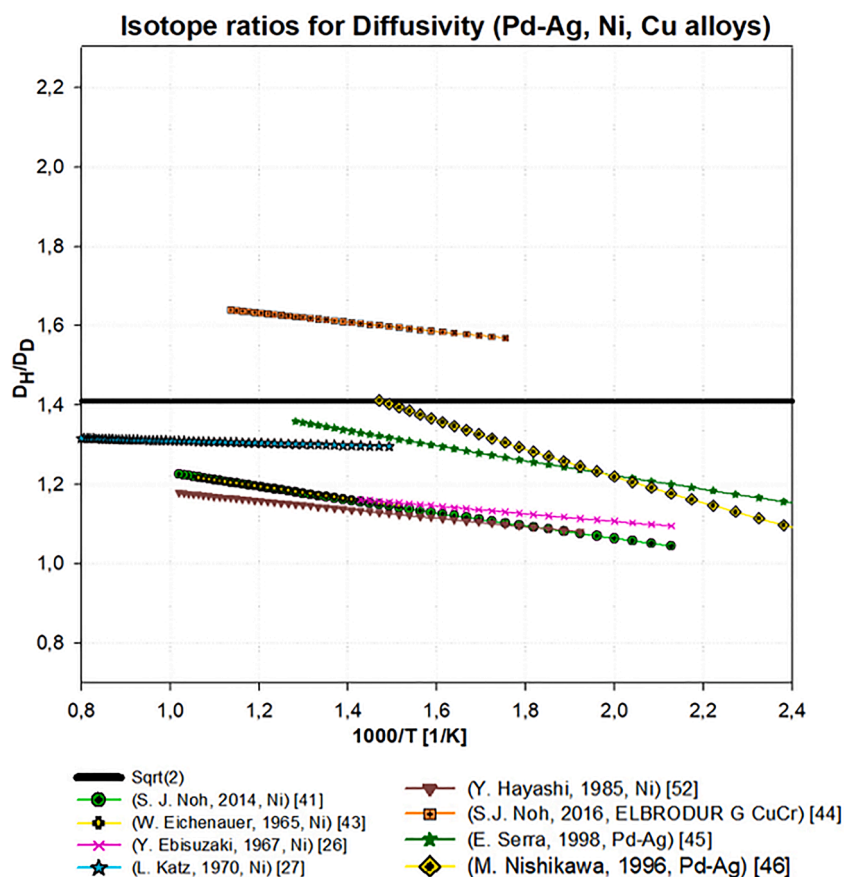
Fig. 3. Isotope Ratios for Diffusivity (Pd-Ag, Ni, Cu alloys).

carried out, that the classical ratio, in terms of absolute value, is not fulfilled in general either. In the case of the isotopic ratio of permeabilities, the majority of cases have a value higher than the theoretical one: between 1.4 and 1.7 in 70% of the analyzed cases.

For the diffusivities, the same can be said: the classical isotope ratio is not generally fulfilled. In this case, 65 % of the curves that represent the isotope effect take values between 1.1 and 1.4 for the tested temperatures.

There are several theories that try to make sense of the large variability of the existing results.

According to some authors, the possible explanation is that the classical equation does not take into account some quantum effects [14], so it is logical that it does not fulfil in reality. Therefore, different quantum statistical approaches to the interaction between the diffusing atom and the host atom have been developed. Quantum effects in the harmonic approximation have been treated by several authors, such as LeClaire [60], Ebisuzaki [26] Franklin [61], Esteban [16,34,48,62–65], Byeon [36,44] or Nakamura [66]. It can be explained as follows: while the classical theory considered the possible energies of the H atom to be continuous, in fact the atom would only be able to occupy certain discrete energy states. Therefore, quantum-statistical partition functions were introduced into the description of the diffusion rate [65]. On this basis, an extrapolation model of the transport parameters of the isotopes was developed, in which the system can be solved using three values: either the diffusivities and solubilities of two isotopes (and deducing the values of the third), or the three diffusivities of the three isotopes (and deducing the solubilities of the three).

However, this solution presents two disadvantages. On the one hand, data are usually available only for protium and deuterium, so it would be necessary to solve the system with the diffusivity and solubility values of both; thus, it is difficult to see how accurate the results are in

predicting the characteristics of the third isotope, since there is nothing to compare with. Precisely, the need to reach relevant conclusions regarding the isotope effect comes from the need not to experiment with tritium, and therefore, if its values were needed to check such validity, this would be somewhat contradictory. On the other hand, Ebisuzaki developed this method based on nickel, a material with fcc microstructure, and thus assuming diffusion as direct jumps from one octahedral site to another. Considering what has been observed when representing different materials and their different trends according to the microstructure presented, it would be totally incorrect to apply this model to other materials without adjusting this issue.

In addition, looking at the results, one can also reflect on another idea. The existence of heterogeneities in the microstructure, such as grain boundary dislocations, inclusions, precipitates and other inherent imperfections in the material, give rise to so-called hydrogen traps. These are places where hydrogen is likely to be "trapped". The effect of traps, as logic dictates, increases the amount of gas absorbed, so their existence will lead to an increase in the Sieverts constant (K_s). At the same time, the transport dynamics will slow down, resulting in a decrease of the diffusivity (D); whereas, in theory, it does not affect the permeability [38,47]. The trapping phenomenon is more important at low temperatures (the limit is set at 573 K according to values obtained in various studies [36,65]) and, in fact, at sufficiently high temperatures its effect will be completely negligible [49]. Taking into account, therefore, that trapping will affect the diffusivity at these temperatures, it is evident that this is a factor that will affect the isotopic relationship between these quantities, and that it would therefore be necessary to take into account in the analyses prior to relating the equations of each of the isotopes themselves. Since the present work is a literature review, there is not enough data to carry it out, but it is necessary to emphasize the need to study it in order to obtain really accurate results. However,
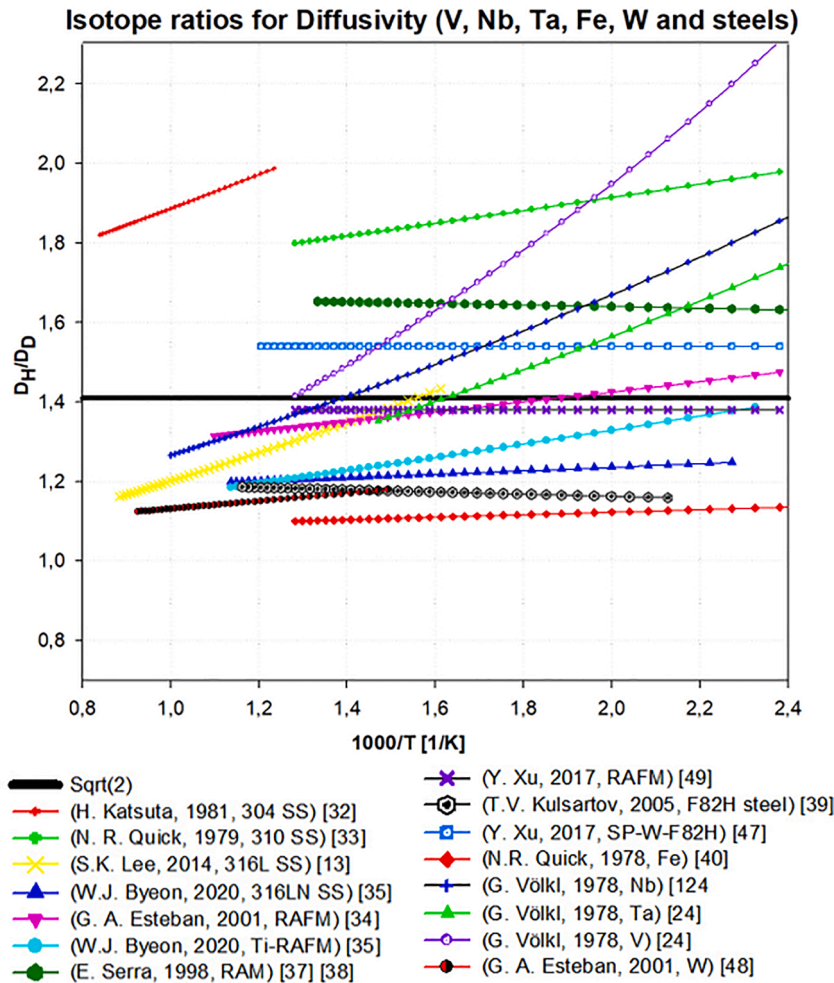
Fig. 4. Isotope ratios for Diffusivity (V, Nb, T, Fe, W and steels).

looking at the results in Fig. 2, it can be seen how the experimental curves of different authors tend to have closer values to each other at higher temperatures and to deviate even more from each other at lower temperatures.

In addition to the trapping effect on diffusivity itself, authors such as Nakamura [53] claim that in their tests, the isotope effect could also affect the trapping parameter and vice versa, so this could be one of the reasons for the observed isotope effect on diffusivity and a new line of research: the interdependence of isotope effect and trapping themselves. So far, there is no definite conclusion on the isotopic influence on trapping, but several general trends can be observed. In studies with bcc microstructures such as martensitic steels [16,36] or W [48], the trapping parameters turn out to have higher trapping energies for heavier isotopes; the same trend has been observed for the diffusion activation energies in most of these microstructures. No studies concerning this effect have been found for fcc microstructures. Therefore, although the relationship between the isotope effect and trapping is not very clear, it seems obvious that the latter should be taken into account when evaluating the former, and therefore ignoring it could be another possible cause for the non-fulfilment of the classical value.

To conclude, it should be noted that several global ideas can be obtained directly from the literature review. On the one hand, the classical ratio is not fulfilled between protium and deuterium: the permeability ratios take higher values than it and the diffusivities, lower; indirectly it is deduced that the Sieverts constant will not be independent of the isotopic ratio, contradicting the theory. In addition, it can be stated that the activation energies are not independent either, which translates into

a dependence on temperature, sometimes high and sometimes weak. The relationship of trapping with temperature should be emphasized, since the diffusivity ratio curves tend to approach at high temperatures and disperse even more at low temperatures.

As for the deviations, on the one hand, the direct relationship with the type of material is contrasted, since different authors publish very similar results analysing the same material. This is observed in the case of nickel [26,41,43,52] and steels [33,36–38]. However, there are also results that differ quite a lot from each other, even using the same material, which confirms the effect of other factors beyond the material itself in the study of the isotope effects. In addition to this, the relationship of the deviations with the microstructure is contrasted, highlighting again the total coincidence of the bcc materials.

Finally, regarding these possible factors outside the type of material and its microstructure, which can no longer be obtained directly from the literature review, several ideas are proposed, such as the possible deviation due to quantum effects or the interdependence of the trapping with the isotope effect.

6. Conclusions

Thanks to the present work, it can be stated that although the classical isotope ratio has been used for years to relate the transport parameters of different isotopes, this prediction is not always correct, at least in the case of hydrogen. The theory is not fulfilled neither in terms of its absolute value($\sqrt{2}$), nor in terms of no effect on solubility, nor in terms of the independence of the activation energies. Moreover, in

general, the permeability ratios take higher values and the diffusivities lower.

In addition, it can be confirmed that this relationship varies depending on the material used, finding similar trends between the same metals published by different authors. Additionally, the idea of the opposite trends of the diffusivity ratios when comparing fcc and bcc materials and the complete coincidence in bcc stands out.

However, by finding different values for the same materials, it is confirmed that there are more factors that may be affecting the isotope effect, and that this does not depend only on the material or its microstructure. On the one hand, it could be due to the inaccuracy of the classical theory due to quantum effects, as some authors have expressed. On the other hand, the interdependence in itself of the trapping with the isotope effect, especially at low temperatures: considering that, the isotopic ratio clearly depends on the temperature and the trapping as well, it is important to take into account this possibility. In this aspect, it should be emphasized the tendency of the curves to approach each other at high temperatures and to disperse even more at low temperatures, which could be related to the trapping effect, since it is known that its affection occurs at low temperatures.

These concepts are proposed as possible explanations and starting points for future studies in the field of the isotope effect, emphasizing the material and microstructure factor, which is the one demonstrated by the present literature review. Therefore, the study of the same material independently is proposed, in order to eliminate this variable and to be able to analyse in detail the effect of other factors.

CRediT authorship contribution statement

María Urrestizala: Conceptualization, Investigation, Resources, Writing – original draft, Formal analysis. **Jon Azkurreta:** Investigation, Validation, Writing – original draft. **Natalia Alegría:** Supervision, Writing – review & editing, Data curation, Funding acquisition. **Igor Peñalva:** Visualization, Supervision, Writing – review & editing, Data curation, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All the information used is properly referenced, so it can be freely consulted.

Acknowledgments

References

[1] E.E. Bloom, D.L. Smith, Structural materials for fusion reactor blanket systems, J. Mater. Energy Syst. 7 (2) (1985) 181–192, https://doi.org/10.1007/BF02833563.

[2] J. Yamabe, S. Matsuoka, Y. Murakami, Surface coating with a high resistance to hydrogen entry under high-pressure hydrogen-gas environment, Int. J. Hydrog. Energy 38 (24) (2013) 10141–10154, https://doi.org/10.1016/j.ijhydene.2013.05.152. https://www.sciencedirect.com/science/article/pii/S0360319913013840.

[3] C.S. Marchi, B.P. Somerday, S.L. Robinson, Permeability, solubility and diffusivity of hydrogen isotopes in stainless steels at high gas pressures, Int. J. Hydrog. Energy 32 (1) (2007) 100–116, https://doi.org/10.1016/j.ijhydene.2006.05.008. https://www.sciencedirect.com/science/article/pii/S0360319906001753.

[4] R.A. Causey, R.A. Karnesky, C. San Marchi, 4.16 - tritium barriers and tritium diffusion in fusion reactors. Comprehensive Nuclear Materials, Elsevier, Oxford, 2012, pp. 511–549, https://doi.org/10.1016/B978-0-08-056033-5.00116-6. R. J. M. Konings, Ed. https://www.sciencedirect.com/science/article/pii/B9780080560335001166.

[5] P. Sabharwall, H. Schmutz, C. Stoots, G. Griffith, Tritium production and permeation in high-temperature reactor systems, in: Proceedings of the *ASME 2013 Heat Transfer Summer Conference Collocated with the ASME 2013 7th International Conference on Energy Sustainability and the ASME 2013 11th International Conference on Fuel Cell Science, Engineering and Technology*, 2013, https://doi.org/10.1115/HT2013-17036. V004T19A001.

[6] D.R. Hanchar, M.S. Kazimi, A tritium permeation model for conceptual fusion reactor designs, J. Fusion Energy 3 (1) (1983) 47–61, https://doi.org/10.1007/BF01053467.

[7] M. Rubel, Structure materials in fusion reactors: issues related to tritium, radioactivity and radiation-induced effects, Fusion Sci. Technol. 57 (2T) (2010) 474–482, https://doi.org/10.13182/FST10-A9438.

[8] J.V. Vas, J.Q. Pan, N.L. Wang, J.H. Xu, R. Medwal, M. Mishra, J.Y. Pae, M. Matham V, L.C.K. Paul, R.S. Rawat, Plasma processed tungsten for fusion reactor first-wall material, J. Mater. Sci. 56 (17) (2021) 10494–10509, https://doi.org/10.1007/s10853-021-05917-y.

[9] R.J. Kurtz, G.R. Odette, Chapter 3 - overview of reactor systems and operational environments for structural materials in fusion reactors. Structural Alloys for Nuclear Energy Applications, Elsevier, Boston, 2019, pp. 51–102, https://doi.org/10.1016/B978-0-12-397046-6.00003-4. G. R. Odette and S. J. Zinkle, Eds. https://www.sciencedirect-com.ehu.idm.oclc.org/science/article/pii/B9780123970466000034.

[10] J.M. Chen, V.M. Chernov, R.J. Kurtz, T. Muroga, Overview of the vanadium alloy researches for fusion reactors, J. Nucl. Mater. 417 (1–3) (2011) 289–294, https://doi.org/10.1016/j.jnucmat.2011.02.015.

[11] R. Arnoux, "Deuterium: a precious gift from the Big Bang," Iter Newsline, vol. 167, (2011), 2011. Available: https://www.iter.org/newsline/167/631.

[12] C. Wert, C. Zener, Interstitial atomic diffusion coefficients, Phys. Rev. 76 (8) (1949) 1169–1175, https://doi.org/10.1103/PhysRev.76.1169. https://link.aps.org/doi/10.1103/PhysRev.76.1169.

[13] S.K. Lee, S. Yun, H.G. Joo, S.J. Noh, Deuterium transport and isotope effects in type 316L stainless steel at high temperatures for nuclear fusion and nuclear hydrogen technology applications, Curr. Appl. Phys. 14 (10) (2014) 1385–1388, https://doi.org/10.1016/j.cap.2014.08.006. https://www.sciencedirect.com/science/article/pii/S1567173914002478.

[14] K.S. Forcey, D.K. Ross, J.C.B. Simpson, D.S. Evans, Hydrogen transport and solubility in 316L and 1.4914 steels for fusion reactor applications, J. Nucl. Mater. 160 (2) (1988) 117–124, https://doi.org/10.1016/0022-3115(88)90038-4. https://www.sciencedirect.com/science/article/pii/0022311588900384.

[15] C.S. Marchi, B.P. Somerday, S.L. Robinson, Permeability, solubility and diffusivity of hydrogen isotopes in stainless steels at high gas pressures, Int. J. Hydrog. Energy 32 (1) (2007) 100–116, https://doi.org/10.1016/j.ijhydene.2006.05.008.

[16] G.A. Esteban, F. Legarda, L.A. Sedano and A. Perujo, "Tritium transport characterisation in martensitic steels from isotopic effect studies," Null, vol. 41, (3), pp. 948–953, 2002. Available: doi:10.13182/FST02-A22725.

[17] M. Shimada, R.J. Pawelko, Tritium permeability in polycrystalline tungsten, Fusion Eng. Des. 146 (2019) 1988–1992, https://doi.org/10.1016/j.fusengdes.2019.03.083. https://www.sciencedirect.com/science/article/pii/S0920379619304041.

[18] M. Shimada, 6.08 - tritium transport in fusion reactor materials☆. Comprehensive Nuclear Materials (Second Edition), Elsevier, Oxford, 2020, pp. 251–273, https://doi.org/10.1016/B978-0-12-803581-8.11754-0. R. J. M. Konings and R. E. Stoller, Eds. https://www.sciencedirect.com/science/article/pii/B9780128035818117540.

[19] G.R. Longhurst, The INEL tritium research facility, Fusion Eng. Des. 12 (3) (1990) 403–409, https://doi.org/10.1016/0920-3796(90)90013-V. https://www.sciencedirect.com/science/article/pii/092037969090013V.

[20] S. Welte, U. Besserer, D. Osenberg, J. Wendel, Tritium laboratory karlsruhe: administrative and technical framework for isotope laboratory operation, Fusion Sci. Technol. 67 (3) (2015) 635–638, https://doi.org/10.13182/FST14-T98.

[21] Anonymous. *Tritium facility*. 2023. Available: https://www.cnl.ca/facilities/tritium-facility/.

[22] T. Hayashi, H. Nakamura, Y. Kawamura, Y. Iwai, K. Isobe, M. Yamada, T. Suzuki, R. Kurata, M. Oyaizu, Y. Edao, T. Yamanishib, Recent progress on tritium technology research and development for a fusion reactor in Japan atomic energy agency, Fusion Sci. Technol. 67 (2) (2015) 365–370, https://doi.org/10.13182/FST14-T31.

[23] S. Alberici, S. Tominetti, Hydrogen transport parameters in metal lattices: a comparison between desorption and permeation mesurement techniques, in: Proceedings of the *ATI-Associazione Termotecnica Italiana-50th Congress*, 1995, pp. 619–630.

[24] J. Völkl, G. Alefeld, Diffusion of hydrogen in metals. Hydrogen in Metals I: Basic Properties, Springer Berlin Heidelberg, Berlin, Heidelberg, 1978, pp. 321–348, https://doi.org/10.1007/3540087052_51. G. Alefeld and J. Völkl, Eds.

[25] T. Shiraishi, M. Nishikawa, T. Yamaguchi, K. Kenmotsu, Permeation of multi-component hydrogen isotopes through austenitic stainless steels, J. Nucl. Mater. 273 (1) (1999) 60–65, https://doi.org/10.1016/S0022-3115(99)00018-5. https://www.sciencedirect.com/science/article/pii/S0022311599000185.

[26] Y. Ebisuzaki, W.J. Kass, M. O'Keeffe, Isotope effects in the diffusion and solubility of hydrogen in nickel, J. Chem. Phys. 46 (4) (1967) 1373–1378, https://doi.org/10.1063/1.1840859. https://aip.scitation.org/doi/10.1063/1.1840859.

[27] L. Katz, M. Guinan, R.J. Borg, Diffusion of H2, D2, and T2 in al Ni and Cu, Phys. Rev. B 4 (2) (1971) 330–341, https://doi.org/10.1103/PhysRevB.4.330. https://link.aps.org/doi/10.1103/PhysRevB.4.330.

[28] W.M. Robertson, Hydrogen permeation, diffusion and solution in nickel, Int. J. Mater. Res. 64 (6) (1973) 436–443, https://doi.org/10.1515/ijmr-1973-640606.

[29] S.A. Steward, "Review of hydrogen isotope permeability through materials," in *Lawrence Livermore National Laboratory Report UCRL-53441,* 1983, doi:10.2172/5277693.

[30] R.A. Anderl, M.R. Hankins, G.R. Longhurst, R.J. Pawelko, Deuterium transport in Cu, CuCrZr, and Cu/Be, J. Nucl. Mater. 266-269 (1999) 761–765, https://doi.org/10.1016/S0022-3115(98)00878-2. https://www.sciencedirect.com/science/article/pii/S0022311598008782.

[31] O. Gautsch, G. Hoddap, Deuterium permeability of the austenitic stainless steel AISI 316, J. Nucl. Mater. 152 (1) (1988) 35–40, https://doi.org/10.1016/0022-3115(88)90138-9. https://www.sciencedirect.com/science/article/pii/0022311588901386.

[32] H. KATSUTA, K. FURUKAWA, Hydrogen and deuterium transport through Type 304 stainless steel at elevated temperatures, J. Nucl. Sci. Technol. 18 (2) (1981) 143–151, https://doi.org/10.1080/18811248.1981.9733235.

[33] N.R. Quick, H.H. Johnson, Permeation and diffusion of hydrogen and deuterium in 310 stainless steel, 472K to 779K, Metall. Trans. A 10 (1) (1979) 67–70, https://doi.org/10.1007/BF02686408.

[34] G.A. Esteban, L.A. Sedano, A. Perujo, K. Douglas, Study of isotope effects in the hydrogen transport of an 8% CrWVTa martensitic steel, Phys. Status Solidi A Appl. Res. 184 (2) (2001) 409–418.

[35] W.J. Byeon, S.K. Lee, S.J. Noh, Transport of hydrogen and deuterium in 316LN stainless steel over a wide temperature range for nuclear hydrogen and nuclear fusion applications, Int. J. Hydrog. Energy 45 (15) (2020) 8827–8832, https://doi.org/10.1016/j.ijhydene.2020.01.130. https://www.sciencedirect.com/science/article/pii/S0360319920302822.

[36] W.J. Byeon, S. Yoon, H. Seo, H.S. Kim, C. Lee, S.K. Lee, B. Chung, S.J. Noh, Hydrogen-isotope transport in Ti-added reduced activation ferritic/martensitic steel, Fusion Eng. Des. 158 (2020) 111849, https://doi.org/10.1016/j.fusengdes.2020.111849. https://www.sciencedirect.com/science/article/pii/S0920379620303975.

[37] E. Serra and G. Benamati, "Hydrogen behaviour in aged low activation martensitic steel F82H for fusion reactor applications," Null*, vol. 14, (6),* pp. 573–578, 1998. Available: doi:10.1179/mst.1998.14.6.573.

[38] E. Serra, A. Perujo, G. Benamati, Influence of traps on the deuterium behaviour in the low activation martensitic steels F82H and Batman, J. Nucl. Mater. 245 (2) (1997) 108–114, https://doi.org/10.1016/S0022-3115(97)00021-4. https://www.sciencedirect.com/science/article/pii/S0022311597000214.

[39] T.V. Kulsartov, K. Hayashi, M. Nakamichi, S.E. Afanasyev, V.P. Shestakov, Y. V. Chikhray, E.A. Kenzhin, A.N. Kolbaenkov, Investigation of hydrogen isotope permeation through F82H steel with and without a ceramic coating of Cr2O3–SiO2 including CrPO4 (out-of-pile tests), Fusion Eng. Des. 81 (1) (2006) 701–705, https://doi.org/10.1016/j.fusengdes.2005.07.019. https://www.sciencedirect.com/science/article/pii/S0920379605005740.

[40] N.R. Quick, H.H. Johnson, Hydrogen and deuterium in iron, 49–506°C, Acta Metall. 26 (6) (1978) 903–907, https://doi.org/10.1016/0001-6160(78)90041-X. https://www.sciencedirect.com/science/article/pii/000161607890041X.

[41] S.J. Noh, S.K. Lee, H.S. Kim, S. Yun, H.G. Joo, Deuterium permeation and isotope effects in nickel in an elevated temperature range of 450–850°C, Int. J. Hydrog. Energy 39 (24) (2014) 12789–12794, https://doi.org/10.1016/j.ijhydene.2014.06.038. https://www.sciencedirect.com/science/article/pii/S0360319914016796.

[42] T. Shiraishi, M. Nishikawa, T. Fukumatsu, Permeation of multi-component hydrogen isotopes through nickel, J. Nucl. Mater. 254 (2) (1998) 205–214, https://doi.org/10.1016/S0022-3115(97)00362-0. https://www.sciencedirect.com/science/article/pii/S0022311597003620.

[43] W. Eichenauer, W. Löser, H. Witte, Löslichkeit und diffusionsgeschwindigkeit von wasserstoff und deuterium in einkristallen aus nickel und kupfer, Int. J. Mater. Res. 56 (5) (1965) 287–293, https://doi.org/10.1515/ijmr-1965-560504.

[44] S.J. Noh, W.J. Byeon, H.W. Shin, H.S. Kim, J. Kim, S.K. Lee, J. Kim, Hydrogen-isotope transport in an ELBRODUR G CuCrZr alloy for nuclear applications in heat sinks, J. Nucl. Mater. 473 (2016) 112–118, https://doi.org/10.1016/j.jnucmat.2016.01.035. https://www.sciencedirect.com/science/article/pii/S0022311516300319.

[45] E. Serra, M. Kemali, A. Perujo, D.K. Ross, Hydrogen and deuterium in Pd-25 Pct Ag alloy: permeation, diffusion, solubilization, and surface reaction, physical

Metallurgical and Materials Science, Metall. Mater. Trans. 29A (3A) (1998) 1023, https://ehu.idm.oclc.org/login?url=https://www.proquest.com/scholarly-journals/hydrogen-deuterium-pd-25-pct-ag-alloy-permeation/docview/213701328/se-2?accountid=17248.

[46] M. NISHIKAWA, T. SHIRAISHI, Y. KAWAMURA, T. TAKEISHI, Permeation rate of hydrogen isotopes through palladium- silver alloy, J. Nucl. Sci. Technol. 33 (10) (1996) 774–780, https://doi.org/10.1080/18811248.1996.9732002.

[47] Y. Xu, Y. Hirooka, N. Ashikawa, T. Nagasaka, Hydrogen isotopes transport in sputter-deposited tungsten coatings, Fusion Eng. Des. 125 (2017) 239–244, https://doi.org/10.1016/j.fusengdes.2017.07.021. https://www.sciencedirect.com/science/article/pii/S0920379617307615.

[48] G.A. Esteban, A. Perujo, L.A. Sedano, K. Douglas, Hydrogen isotope diffusive transport parameters in pure polycrystalline tungsten, J. Nucl. Mater. 295 (1) (2001) 49–56, https://doi.org/10.1016/S0022-3115(01)00486-X.

[49] Y. Xu, Y. Hirooka, T. Nagasaka, Bi-directional hydrogen isotopes permeation through a reduced activation ferritic steel F82H, Fusion Eng. Des. 125 (2017) 343–348, https://doi.org/10.1016/j.fusengdes.2017.04.022. https://www.sciencedirect.com/science/article/pii/S0920379617304258.

[50] A. Aiello, I. Ricapito, G. Benamati and R. Valentini, "Hydrogen isotopes permeability in Eurofer 97 martensitic steel," Null*, vol. 41, (3),* pp. 872–876, 2002. Available: doi:10.13182/FST41-872.

[51] S.J. Noh, S.K. Lee, W.J. Byeon, Y.B. Chun, Y.H. Jeong, Transport of hydrogen and deuterium in the reduced activation martensitic steel ARAA, Fusion Eng. Des. 89 (11) (2014) 2726–2731, https://doi.org/10.1016/j.fusengdes.2014.07.013. https://www.sciencedirect.com/science/article/pii/S0920379614004657.

[52] Y. Hayashi and A. Tahara, "Hydrogen isotope permeation through iron and nickel*," vol. 145, (1–2),* pp. 261–268, 1985. Available: doi:10.1524/zpch.1985.145.1_2.261.

[53] H. Nakamura, T. Hayashi, T. Kakuta, T. Suzuki, M. Nishi, Tritium permeation behavior implanted into pure tungsten and its isotope effect, J. Nucl. Mater. 297 (3) (2001) 285–291, https://doi.org/10.1016/S0022-3115(01)00635-3. https://www.sciencedirect.com/science/article/pii/S0022311501006353.

[54] A.D. Le Claire, Permeation of gases through solids, Defect Diffus. Forum 34 (1) (1983), https://doi.org/10.4028/www.scientific.net/DDF.34.1. https://www.scientific.net/DDF.34.1.

[55] H.K. Perkins, T. Noda, Deuterium transport through 304 and 304L stainless steel at low driving pressures and 15 KeV deuteron bombardment, J. Nucl. Mater. 71 (2) (1978) 349–364, https://doi.org/10.1016/0022-3115(78)90435-X. https://www.sciencedirect.com/science/article/pii/002231157890435X.

[56] M.R. Louthan, R.G. Derrick, Hydrogen transport in austenitic stainless steel, Corros. Sci. 15 (6) (1975) 565–577, https://doi.org/10.1016/0010-938X(75)90022-0. https://www.sciencedirect.com/science/article/pii/0010938X75900220.

[57] A.M. Stoneham, Non- classical diffusion processes, J. Nucl. Mater. 69-70 (1978) 109–116, https://doi.org/10.1016/0022-3115(78)90239-8. https://www.sciencedirect.com/science/article/pii/0022311578902398.

[58] H. Wipf, Diffusion of hydrogen in metals. Hydrogen in Metals III: Properties and Applications, Springer Berlin Heidelberg, Berlin, Heidelberg, 1997, pp. 51–91, https://doi.org/10.1007/BFb0103401. H. Wipf, Ed.

[59] A. Pozio, S. Tosti, Pd-Ag electrical resistivity in hydrogen and deuterium: temperature effect, Materials 12 (21) (2019) 10–29, https://doi.org/10.3390/ma12213551 *(Basel),* https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6862056/.

[60] A.D. Le Claire, "Some comments on the mass effect in diffusion," *Null,* vol. 14, (132),* pp. 1271–1284, 1966. Available: doi:10.1080/14786436608224292.

[61] W. Franklin, Phonon theory of solid-state diffusion including anharmonic effects, Phys. Rev. 180 (3) (1969) 682–694, https://doi.org/10.1103/PhysRev.180.682. https://link.aps.org/doi/10.1103/PhysRev.180.682.

[62] G.A. Esteban, A. Perujo, K. Douglas, L.A. Sedano, Tritium diffusive transport parameters and trapping effects in the reduced activating martensitic steel OPTIFER-IVb, J. Nucl. Mater. 281 (1) (1999) 34, https://doi.org/10.1016/s0022-3115(00)00188-4.

[63] G.A. Esteban, F. Legarda, A. Perujo, Isotope effect in hydrogen transport in bcc-structured materials: polycrystalline tungsten and reduced activation ferritic-martensitic steel, Fusion Sci. Technol. 48 (1) (2005) 617–620, https://doi.org/10.13182/FST05-A1001.

[64] G.A. Esteban, A. Perujo and F. Legarda, "Study of the isotope effects in the hydrogen transport in polycrystalline tungsten," *Cross-Disciplinary Applied Research in Materials Science and Technology,* vol. 480, pp. 537–542, 2005. doi:10.4028/www.scientific.net/MSF.480-481.537.

[65] G.A. Esteban, A. Perujo, K. Douglas and L.A. Sedano, "Isotope effects in hydrogen transport parameters in the martensitic steel Optifer-IVb," *European Comission Report En Eur* 19021, pp. 38, 2000. doi:10.1016/s0022-3115(00)00188-4.

[66] H. Nakamura, W. Shu, T. Hayashi, M. Nishi, Tritium permeation study through tungsten and nickel using pure tritium ion beam, J. Nucl. Mater. 313-316 (2003) 679–684, https://doi.org/10.1016/S0022-3115(02)01383-1. https://www.sciencedirect.com/science/article/pii/S0022311502013831.