Influence of True Diffusion Coefficient on Hydrogen Diffusion in Tungsten in the Field of Defects

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Abstract. Numerical calculations of thermal desorption spectra, permeation, and accumulation of hydrogen in radiation damaged tungsten have been made using two approximations for the diffusion coefficient: the commonly used approximation of Fraunfelder and that of Heinola, which he proposed to describe only the most high temperature data of Fraunfelder.

1. Introduction
Accumulation of tritium in radiation defects in tungsten divertor plates is one of the major sources of in-vessel tritium inventory in ITER [1,2]. Predictions of tritium inventory and related laboratory experiments on thermal desorption, accumulation and permeation are usually based on computer modelling of hydrogen diffusion in the field of defects. The experimental data on diffusivity obtained by Fraunfelder [3], which were measured in the range of 1100-2400K, are commonly believed to be the most reliable.

\[ D_f(T) = 4.1 \times 10^{-7} \exp(-0.39 \text{ eV}/kT) \text{ m}^2/\text{s}, \] (1)

Contrary to experimental data, theoretical calculations performed using high accuracy first-principles computational methods [4-9] gave the activation energies in the range of \( E_D = 0.17-0.22 \text{ eV} \), though one can find both smaller and higher estimations [7,10,11]. The disagreement between theoretical and experimental \( D(T) \) was suggested to be due influence of defects at low temperatures [5,7,12]. Heinola [5] paid attention that experimental data of Fraunfelder [3] in the range of 1500-2500 K are well approximated by

\[ D_H(T) = 1.58 \times 10^{-7} \exp(-0.25 \text{eV}/kT) \text{ m}^2/\text{s}, \] (2)

which can be considered as a true diffusivity, while two low temperature points at T<1500 K are influenced by defects.

Later calculations [7,12] demonstrated that all experimental data on diffusivity of H in W available from literature can be really well described by the effective diffusion coefficient in the field of defects within the formalism of Mac-Nabb and Foster [13] if to use the true activation energy for diffusion \( E_D = 0.2-0.25 \text{ eV} \) and several sets of binding energies and concentrations of defects.

The uncertainty in the diffusion coefficient rises the question about reliability of calculations of thermal desorption spectra, diffusion profiles, accumulation, and permeation of hydrogen, which are performed
using diffusion codes in application to laboratory experiments and predictions for fusion devices. This paper compares the calculations, which use the two Arrhenius approximations proposed by Fraunfelder (1) and by Heinola (2).

2. Model
For qualitative analyses we use standard one-dimensional diffusion equation with trapping–detrapping term related with defects.

\[ \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} \frac{\partial y}{\partial t} \]  

(3)

where \( u \) is the concentration of hydrogen in interstitials (movable atoms), \( y \) – the concentration of hydrogen in defects (trapped atoms), and \( D \) – the diffusion coefficient given either by (1) or by (2).

The trapping–detrapping term can be written in the simplified form as

\[ \frac{\partial y}{\partial t} = f e^{\frac{E_D}{kT}} u \left( \frac{y-y}{w} \right) - f e^{\frac{E_D+E_b}{kT}} y \]  

(4)

Here \( Y \) is the concentration of defects, \( W \) is the concentration of tungsten atoms, \( f \) – characteristic vibration frequencies of hydrogen atoms, \( E_b \) – the hydrogen-to-defect binding energy, and \( E_{dt} = E_D+E_b \) – the activation energy for tritium release from defects (detrapping energy).

The defects are either distributed uniformly through the depth to model natural and neutron induced damage or uniformly distributed in a layer 50 nm thick near the surface to model ion induced defects. The concentration of defects varied in the range \( Y/W = 10^{-4} \)–\( 10^{-2} \) atomic parts. Typical defects are dislocations, vacancies, and vacancy clusters. Recent TDS experiments gave very accurate values \( E_{dt} = 1.56 \pm 0.06 \) eV for vacancies \[14\] and \( E_{dt} = 2.10 \pm 0.02 \) eV for vacancy clusters \[15\], while detrapping energy from dislocations is smaller \( \approx 0.9 \) eV.

All the calculations were performed using TMAP7 code \[16\] commonly used for calculations of the type.

3. Results
This section demonstrates calculations of thermal desorption spectra, diffusion profiles, and accumulation and permeation dynamics:

3.1. Thermal desorption spectra
The boundary conditions were set to be \( u(0,t) = 0 \) and \( u(L,t) = 0 \) in calculations of thermal desorption spectra to exclude surface effects. The thickness of the sample was 0.5 mm.

Figure 1 shows the example of calculations of thermal desorption spectra (TDS) for three detrapping energies, two diffusion coefficients, and two distributions of defects. For the case of shallow depth distribution of defects (50nm), which is typical for TDS experiments, both approximations for the diffusion coefficient proposed by Fraunfelder (1) and Heinola (2) gave the same TDS in all calculations. Fig 1 gives just one example for very low concentration of defects and their low initial population, where influence of diffusion could be expected. Nevertheless, the difference between the calculations with different \( D(T) \) approximations is negligible for all the three detrapping energies 0.9 eV, 1.6 eV, and 2.1 eV.
The agreement is good in most cases even if defects are uniformly distributed through the depth, though influence of diffusion in this case must be maximal. The difference is observed only if the detrapping energy is small (0.9 eV) and both the concentration of defects and their populations are low. The case of worse agreement is also shown in Figure 1. And even in this case, the difference in the peak positions, which are approximately proportional to $E_b$, is rather small (around 10%) for two $D(T)$ approximations.

One must mention, that the detrapping energies $E_d=E_b+E_D$ but not the binding energies $E_b$ were used in calculations; and in this case calculated TDS are very similar for two different approximations for $D(T)$. This means that the key parameter that can be extracted from comparison of experimental and numerical TDS is the detrapping energy $E_d$, while the value of the binding energy $E_b$, extracted from experimental TDS depends on the value of $E_D$ used in calculations.

3.2. Diffusion profiles

Figure 2 and 3 show examples of the mobile and trapped profiles of hydrogen diffusing from the front side towards the back side at temperatures 2000 K and 700 K, respectively. Parameters are: $L=2$ mm, $u(0,t)/W=10^{-2}$, $Y/W=10^{-4}$, $E_d=1.6$ eV. The approximation of Heinola is slightly less above 1700 K and significantly higher below 1700 K.

The profiles of mobile hydrogen calculated with different $D(T)$ are rather similar at 2000 K (fig.2a). At this temperature, defects are ineffective in trapping, and the profiles of mobile hydrogen are well described by the ordinary diffusion equation. Fraunfelder’s diffusivity is only slightly higher at 2000 K; therefore the respective transient mobile concentration is also only slightly higher in fig.2a. In contrast, the trapped profiles in fig.2b are very different for two $D(T)$ approximations though the detrapping energies are equal and mobile concentrations are nearly the same. The relation between the trapped and mobile concentrations can be qualitatively analyzed using the condition of local equilibrium between mobile and trapped hydrogen, that is the condition $\partial y/\partial t=0$ in (4). It follows from this condition that the mobile and trapped concentrations are proportional at low population of defects ($y<y_0$), and the trapped concentration increases with increase of the binding energy $E_b$ and does not depend on the activation energy for diffusion $E_D$. At the given $E_d=1.6$ eV: the approximation of Heinola gives $E_b=1.35$ eV, while the approximation of Fraunfelder gives $E_b=1.21$ eV. Therefore the trapped concentration is higher for the case the approximation of Heinola is used.

At 700 K defects are active in trapping, and the mobile profiles (fig.3a), which can be described by the effective diffusion coefficient following the McNabb and Foster formalism [23], are different. Defects are nearly saturated closer to the front surface (fig 3b), trapped profiles are stepped, and the step moves toward the back side progressively as defects are filled. The stepwise profile at 700 K is formed due to
active defect trapping, which does not permit hydrogen to diffuse deeper in the bulk until defects are filled at low depths. It is indicative that the positions of fronts of the mobile and trapped profiles are similar in this case. The trapped concentration (fig.3b) is always higher in the case of Heinola’s approximation due to a higher binding energy $E_b$. Transport of hydrogen through the near-surface region, where defects are saturated, is determined by the true diffusion coefficient. Therefore defects are populated faster, trapped profile step moves faster in fig.3b, and the mobile profile becomes longer in fig.3a.

![Figure 2](image1.png)

**Figure 2.** Depth profiles of mobile and trapped hydrogen diffusing from the surface $x=0$ at 2000 K. Circles (marked as F) are for Fraunfelder’s approximation; squares (marked as H) are for Heinola’s approximation. Open symbols are for $t=6$ s (transient profiles); closed symbols are for $40$ s (steady state profiles). Other parameters are: $E_d=1.6$ eV, $Y/W=10^{-4}$, $u_d/W=10^{-7}$.

![Figure 3](image2.png)

**Figure 3.** Depth profiles of mobile and trapped hydrogen diffusing from the surface $x=0$ at 700 K. Parameters are the same as in fig.2.

3.3. Accumulation

The number of hydrogen atoms in solution is usually very low, and accumulation in presence of defects is determined mainly by defect trapping. Figure 4 shows the time dependencies of accumulation of hydrogen in a sample at $E_d=1.6$ eV, $T=700$ K and $T=2000$ K. All parameters were the same as those used for calculation of profiles given in fig.2 and fig.3. One can see that the amount of accumulated hydrogen is higher in calculations with Heinola’s approximation; and this correlates with the features of the concentration profiles discussed above.

The shapes of the curves are different at temperatures 700 K and 2000 K. At low temperature the transition to saturation is rather sharp, while at high temperature the accumulation steadily grows with time. These features follow from depth profiles in fig.4. At 700 K, the front of the trapped profile looks like a step, which moves to the back side, so the transition to saturation is to be rather sharp, while at 2000 K, the concentration at any depth smoothly increases in time until the steady state is achieved.
Figure 4. Accumulation of hydrogen in defects as a function of time during diffusion from side x=0. The sample thickness is 2 mm. Two approximations for the diffusion coefficient are used. Trap concentration Y=10^{-4} ap, mobile concentration \( u_0 = 10^{-7} \) ap, detrapping energy \( E_{dt} = 1.6 \) eV. Temperatures: a) \( T=700 \) K, b) \( T=2000 \) K.

3.4. Permeation

Figure 5 gives examples of time dependencies of the permeation rates, which are calculated using approaches of Heinola and Fraunfelder. One can see that these permeation rates are different both at low and high temperatures. The permeation rate equals the gradient of concentration of mobile hydrogen at the back side of the sample multiplied by the true diffusion coefficient. The steady state profiles of movable hydrogen are identical in fig 2a, but diffusion coefficients are different. Therefore, permeation at 700 K is higher if the diffusion coefficient of Heinola is used as it is higher at low temperatures, while permeation at 2000 K is higher if the diffusion coefficient of Fraunfelder is used as it is higher at high temperatures.

The lag time of permeation in the field of defects is determined by the effective diffusion coefficient. At high temperatures (2000 K), defects are ineffective in retarding diffusion, and the effective diffusion coefficient equals the true diffusion coefficient. The diffusion coefficients of Heinola and Fraubfelder are very similar at high temperatures, therefore profiles of mobile concentrations at 2000 K in fig 2 are very similar, and lag times of two permeation curves in fig.5b are about the same. At small temperatures (700 K), lag times are very different (fig.5a). This correlates with the difference in profiles in fig.3. If Heinola’s approximation is used in calculations, the diffusion front moves faster and hydrogen appears faster on the back side in fig.3, leading to shortening of the permeation lag time in fig.5a.
4. Conclusion

Numerical calculations of thermal desorption spectra, diffusion profiles, accumulation, and permeation of hydrogen in tungsten were compared for two approximations for the diffusion coefficient proposed in literature. One of them is the commonly used approximation of Fraunfelder, which he derived from his experimental data obtained in the temperature range of 1100-2400 K, and which is commonly believed to be the most reliable. Another one is the approximation of Heinola, which describes only the high temperature data of Fraunfelder in the range of 1500-2400 K, and which correlates with several theoretical predictions.

It has been demonstrated that numerically calculated thermal desorption spectra of ion/plasma implanted hydrogen, are very similar for these two approaches if the value of the detrapping energy from defects is fixed. This means that the parameter, which can be correctly extracted from TDS experiments and which must be further used for numerical predictions of hydrogen accumulation and permeation, is the detrapping energy, but not the binding energy. The latter depends on of the activation energy for diffusion used in fitting to experimental TDS.

Contrary to TDS, it has been demonstrated that results of calculations of diffusion, accumulation, and permeation through samples with defects are strongly different for these two approximations for the diffusion coefficient. The approximation of Heinola leads to faster movement of the mobile and trapped profiles, increase of accumulation in defects, decrease of the permeation lag time, and increase of the permeation rate.

The contradiction between experimental and theoretical data on the diffusivity makes the predictions of tritium accumulation in ITER uncertain. Tritium inventories in ITER calculated with the diffusion coefficient proposed by Fraunfelder are underestimated if the approximation of Heinola is correct. There is need in more accurate experimental data on the diffusivity of hydrogen in W in the high temperature region.

5. References

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