

# Theoretical Methods of Hydrogen Diffusion Calculation in Metals Review



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## Abstract

In the review discuss some theoretical methods of hydrogen diffusion calculation in metals. True values of the energy barrier for hydrogen diffusion can be calculated from first principles. The transition from the theoretical values of the energy barrier to the model values of the activation energy is associated with considering additional influencing factors, primarily physical parameters – zero-point energy, decay of local deformation near the hydrogen atom, temperature-dependent potentials, etc. The presentation of the results is greatly influenced by the parameters of the diffusion models used for calculations - the Arrhenius equation, the Einstein formula of molecular dynamics, the Kerr diffusion equation, the operator expression of quantum statistical mechanics, and diffusion equation of statistical thermodynamics. The statistical model of H diffusion in FCC metals at a high temperature makes it possible to explain the high values of the pre-exponential factor of H diffusion coefficients. The results of many works show that quantum effects play a decisive role in the H diffusion in metals at low temperatures. Further development of quantum- mechanical theories of diffusion will allow for consideration of the influence of these factors.

**Keywords:** Hydrogen diffusion; Metals; Pre-exponential factor; Statistical model; Quantum effects; Tunneling

## Introduction

The diffusion of hydrogen in metals has received a lot of attention and has been the subject of intensive training in recent decades. First, this is due to the practical interest in using the metal – hydrogen system for a number of technological applications, including the creation of radiation-resistant materials and filters for producing pure hydrogen, for using gas H as a secondary energy carrier, and fusion reactor technology [1,2]. Secondly, it is caused by the undesirable effect of hydrogen on the properties of materials (embrittlement, corrosion, crack propagation) [3,4]. In particular, H diffusion in Fe and Fe alloys is very important because this leads to engineering problems associated with hydrogen embrittlement and degradation of high strength steels, reactor materials, etc [5,6].

Hydrogen atoms have a unique low mass and size in comparison with other interstitial atoms in metals, and for this reason they have an extremely high diffusion mobility [7-10]. The diffusion coefficients of hydrogen in solid metals are almost the same as in liquids. This function, in addition to the small size and mass of the hydrogen atom, is also associated with the dissociation of the hydrogen molecule into individual atoms when it enters the metal [9,10]. In metal crystals, hydrogen atoms are in interstitials

and in the diffusion process they pass from one interstitial site to another. In FCC lattice, hydrogen can occupy two types of interstitial sites: octahedral and tetrahedral. At the present time, the question of the mechanism of hydrogen diffusion in the crystal lattice of metals remains. Even in a pure crystal, transitions between interstitials of different types are possible, which entails, in particular, the ambiguity of the activation energy of hydrogen diffusion. In addition, as noted in [7], the redistribution of hydrogen atoms in interstitial sites of various types due to changes in external conditions, for example, deformation, can lead to a change in the diffusion parameters. It should be noted that other factors may also lead to deviations from the Arrhenius law, in particular, the possibility of diffusion jumps of different lengths and the effect of crystal lattice defects [9,11]. This high diffusion mobility is thought to be the result of a very low activation energy due to the quantum nature of H [11].

Although there has been a significant amount of experimental research on the diffusion of hydrogen (see reviews in [12-15], very little reliable data available, especially on the distribution at temperatures below room. First principles calculations and classical approaches molecular mechanics has been used to

study hydrogen adsorption, absorption, dissolution and diffusion energy in the case of body-centered cubic (BCC) Fe in several papers [16-20]. However, as far as we know, there is no systematic derivation of diffusion coefficients for which statistical and quantum-mechanical effects would be taken into account in a wide temperature range. The use of such calculations is important for understanding the possible mechanisms of hydrogen diffusion in metals.

The purpose of this work is critical review of the theoretical methods of hydrogen diffusion calculation in metals.

## Results and Discussion

The classical atomic theory of diffusion gives an expression for the diffusion coefficient self-diffusion. In early works on the statistical theory Ya.I. Frenkel and his followers, the dependence of the diffusion coefficient on the square of the distance between two atomic positions was obtained [21-24]. This expression for the diffusion coefficient is also commonly used in modern molecular dynamics [16-20]. However, due to a significant discrepancy between the calculated and experimental data, even in these classical works, additional parameters were introduced to calculate the diffusion coefficients. At the same time, it is well known, that the main driving forces of diffusion in non-equilibrium thermodynamics are the gradients of chemical potentials  $\mu_i$  of the components of the system [24-26]. This position should be considered when deriving equations for the diffusion coefficient. However, it is very difficult to introduce chemical potentials into the diffusion equations in the atomic model [26-28].

In the classical limit and using the random-walk model of interstitial diffusion in a BCC lattice,  $D_0$  in the Arrhenius expression for the diffusion parameter  $D = D_0 \exp(-E_a / RT)$  can be represented as [17]:

$$D_0 = \frac{n\Delta^2}{6} \frac{\prod_{j=1}^{3N} \nu_j}{\prod_{j=1}^{3N} \nu_j^+} \quad (1)$$

where,  $n$  is a geometrical factor for the number of equivalent jump paths,  $\Delta$  is the jump length, and  $\nu_j$  and  $\nu_j^+$  are the real normal mode frequencies at the initial state and the transition state, respectively. Close to the room temperature is necessary to account for quantum correlations to the diffusion barrier i.e. the discreteness of H vibrational modes in the metal lattice [17].

Kebr presented another description of H diffusion, assumed, that the lattice vibrations are the same minimum energy and saddle-point configurations. For BCC metals at room temperature the limit of  $h\nu_H \gg k_B T$ , where  $\nu_H$  is the frequency of the localized H vibrational modes. In this limit the pre-exponential factor can be represented as [17]:

$$D_0 = \frac{n\Delta}{6} \frac{k_B T}{h} \exp\left[\frac{-\Delta E + \Delta ZPE}{k_B T}\right] \quad (2)$$

Where  $\Delta E$  is the energy difference between the saddle point and minimum energy configuration on the potential energy surface,  $\Delta ZPE$  is the difference in zero-point energies. Thus, the exponential term  $(\Delta E + \Delta ZPE)$  in Eq. 2 is a ZPE-corrected diffusion barrier. Moreover, we can see that the pre-exponential factor in Eq. 2 is temperature dependent to the first degree.

In [28] it is proposed to use statistical model expressions for the pre-exponential coefficient. This approach, based on the first principles of statistical thermodynamics, makes it possible to adequately consider the statistical distribution of impurity atoms according to their energy.

In this case the diffusion coefficient for impurity atoms in metals is equal to [28]:

$$D = \frac{2\pi m k^2 T^2 d}{h^3} e^{-W_0/kT}, W_0 = U - \mu_0 \quad (3)$$

$U$  is the potential barrier height of the diffusion process,  $\mu_0$  is the chemical potential of impurity atoms, and pre-exponential factor after transformations is [28]:

$$D_0 = \frac{2\pi N_e^2 m_a k^2 T^2 d}{h^3 N \rho} \quad (4)$$

where  $d$  – distance between two nearest identical position sites of impurity particles

$N$  is the Avogadro number ( $\text{mol}^{-1}$ )

$k$  - Boltzmann constant

$h$  - Planck constant

$N_e$  is the atomic number of the diffusive impurity atoms (1 for H)

$m_a$  is the atomic mass unit (H).

$\rho$  is the metal density.

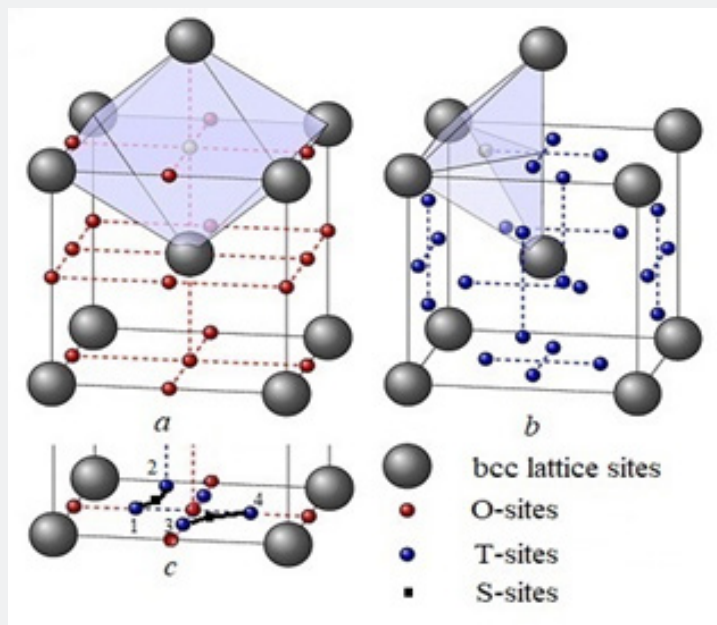
Expression (4) of the statistical model significantly differs from the expressions used in simple molecular dynamics [16-20]. The interplanar distance  $d$  enters this expression to the first degree. But this formula assumes the dependence of  $D_0$  on the square of the atomic number of the diffusing element and the square of the temperature.

In [25] had been found that H in BCC metals, V, Nb and Ta, had a preference to occupy T-sites, but O-sites in FCC-Pd, which could be correlated qualitatively with protonic electrostatic potential in pure bulk metals.

If consider the movement of a hydrogen atom between tetrahedral sites, the most probable trajectory for the migration of a hydrogen atom from one T-site into the nearest-neighbor

T-site is via a S-site how (Figure 1). In [17] it was found that H does not utilize a straight – line trajectory, but rather hops from one T-site to a nearby T-site by a curved path distorted towards

an O-site. The S-site is set like a saddle point along the minimum energy path (MEP) for direct hopping of an H atom between two neighboring T-sites [11].



**Figure 1:** Positions of O-sites (a) and T-sites (b) of the BCC lattice. The S-sites are the saddle point along the MEP [11,17] for direct hopping of aH atom between two neighboring T-sites (paths 1-2 and 3-4 respectively) (c) [42].

Despite a significant number of experimental studies of quantum hydrogen diffusion in metals (see also [29-35]), there are very few reliable data, especially on the hydrogen distribution at temperatures below room temperature. Experimental data on quantum diffusion of hydrogen have been obtained for Nb and Ta [28,29] and in Na and K for deuterium [30,31].

Theory of hydrogen diffusion in metals has been developed by various models, namely: the small polaron model of Flynn and Stoneham [34, 36, 37], semiclassical transition state theory [37], Feynman path-integral molecular dynamics model [13,38], density functional theory (DFT) [35,38] centroid and ring polymer molecular dynamics, [39], statistical thermodynamics [40-42], and others. In quantum theories of diffusion, the interpretation of bends on the  $D(T)$  dependences in Ta and Nb [34,35,40] was successful.

Ab initio DFT calculations of diffusion activation energies for both migration mechanisms were performed, which showed excellent agreement with experimental data for H in Nb and Ta [40]. In work [41] was presented the statistical model of H diffusion in FCC metals at a high temperature (900 - 2000 K). This thermodynamics model makes it possible to explain the high values of the pre-exponential factor of H diffusion coefficients ( $\sim 10^{-7} \text{ m}^2\text{s}^{-1} - 10^{-6} \text{ m}^2\text{s}^{-1}$ ) in FCC metals ( $\gamma$ -Fe, Ni, Pd, Al, Ag) at high

temperature due to the coefficient  $T^2$  in the diffusion equations.

It was shown in [11,41] that the diffusion of hydrogen in  $\alpha$ -iron deviates from the Arrhenius equation, which is an additional indication of the dependence of diffusion coefficients on temperature. In [11] the centroid path-integral molecular dynamics method (CMD) was used to change free energy profiles for H migration at various temperatures see (Figure 1) in [13]. According to these data, at temperatures below 300 K, hydrogen diffusion can occur both through S-sites and O-sites with similar potential barrier values.

It was proposed to use the statistical model for a more accurate calculation of the hydrogen diffusion in BCC metals at low temperatures [42]. The calculations performed are compared with the known experimental data on the diffusion of hydrogen atoms in  $\alpha$ -Fe with a good agreement between the results.

It was suggested in [42] that thermally activated fast tunneling transition of hydrogen atoms through the potential barrier at temperatures below 300 K provides an almost free movement of H atoms in the iron lattice. It was also assumed that the patterns of hydrogen diffusion in vanadium manifest themselves in the same way as in iron. The results of many works [28-42] show that quantum effects play a decisive role in the H diffusion in BCC metals at low temperatures. In this case, therefore, the Arrhenius

equation and the Einstein formula do not give a correct description of diffusion at all, and at low temperatures it is necessary to use quantum mechanical models of atomic tunneling.

It is assumed that modern ab initio modeling will provide a good description of the geometry, energy, and potential energy surface in Fe-H systems [31-40]. However, as far as we know, there is no systematic derivation of the diffusion coefficients for which quantum effects are considering in a wide temperature range. The development of such calculations from first principles of quantum mechanics is important for understanding the possible mechanisms of hydrogen diffusion in metals.

## Conclusion

We are deeply convinced that the true value of the energy barrier for hydrogen diffusion can be calculated from the first principles. The transition from the theoretical values of the energy barrier to the model values of the activation energy is associated with considering additional influencing factors, primarily physical parameters – zero-point energy ZPE, decay of local deformation near the hydrogen atom, temperature-dependent potentials, etc.

The presentation of the results is greatly influenced by the parameters of the diffusion models used for calculations - the Arrhenius equation itself, the Einstein formula of molecular dynamics, the Kehr diffusion equation, the operator expression of quantum statistical mechanics, and diffusion equations of statistical thermodynamics.

Undoubtedly, these models do not consider many specific factors affecting the diffusion parameters of atoms in a metal, such as the interaction of impurity atoms, influence of the Debye temperature, quantum tunneling at a low temperature, etc. Further development of quantum- mechanical theories of diffusion will allow for consideration of the influence of these factors.

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