HYDROGEN DIFFUSION – A REVIEW
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2.1 INTRODUCTION

Research on hydrogen in metals and alloys has attracted attention for reasons motivated both from a basic as well as an applied point of view. The possible application of metal-hydrogen systems will be discussed in applied physics [1]. It is useful for the study of the basic interactions leading to phase transitions of H in metals, the change in electronic properties and the hydrogen mobility. Hydrogen in metals has a large mobility. At room temperature and below, its mobility has many orders of magnitude larger than that of other interstitially dissolved atoms. The hydrogen atom, being the lightest of the elements in nature is believed to follow quantum laws as it moves from one lattice site to another, especially at low temperatures [2]. Hydrogen interacts with metallic microstructure in a large number of metals and alloys. The interactions of hydrogen with vacancies, voids, grain boundaries, dislocations and impurity atoms have profound consequences on the mechanical behavior and chemical properties of materials. The knowledge of the permeation of hydrogen through thin metallic membranes is essential for the development of hydrogen selective materials or protecting coatings. This chapter gives a review on the literature of hydrogen diffusion.
In recent years, there has been growing interest in the diffusivity of hydrogen in metals and alloys and a large number of measurements of the diffusivity have been made [3]. Diffusion of hydrogen in solids provides an intriguing and difficult intellectual problem in addition to its practical importance. One of the common aspects of applied research of metal-hydrogen system is to deal with complex material. Metal-hydrogen systems are of continuing interest as physical examples of lattice gas [4]. The properties of metal-hydrogen systems were the subject of intensive research activities over the last decades, motivated by interest in basic science and technological applications [5].

Because of small mass compared to any other interstitial atoms, quantum effects in diffusion are likely to be observed for hydrogen if they occur at all. Hydrogen isotopes have large mass ratios and hence isotopic effects can be studied over a wide range, which is important for determining the distinction between different possible diffusion mechanisms.

At low temperatures, the interstitial is delocalized in the form of a band unless it is trapped by lattice defects. At higher temperatures, the interstitial is localised at a specific interstitial site and the diffusion process is a thermally activated jump from one to another interstitial site via tunneling or hopping over the potential barrier. The second process happens at higher temperature because higher activation energy is required to overcome the barrier. The larger diffusion coefficient D and smaller activation energy $E_a$ are believed to
arise due to the light mass of hydrogen [6]. At very high temperature fluid-like diffusion takes place.

Hydrogen (\(^1\)H) diffusion can be observed at low temperature in which quantum effects in the diffusion of \(^1\)H can be expected. It may be possible that \(^1\)H atoms remain mobile even at zero temperature. In Palladium, it is noticed that heat production below 1K possibly results from a rearrangement of H atoms [7]. Recent Quenching experiment [8] on hydrogen in Tantalum has shown hydrogen mobility at 11K. It is expected that the migration of hydrogen atom proceeds via different mechanisms, one of them predominating over the other in a given range of temperature. A classification of possible mechanisms as a function of temperature is discussed by Fukai and Sugimoto [6].

2.1.1 Palladium – Hydrogen system

Graham first discovered that palladium could absorb large amounts of hydrogen gas [9-10] a century ago. Diffusion aspect of the Pd-H system has been most extensively investigated. The ability to absorb hydrogen is common to all metals because the hydrogen atom is the lightest and smallest of the solute elements and therefore diffuses easily. Palladium is a monomorphc metal with fcc crystal structure. It is a noble metal in the platinum group. Palladium has high stability, adequate heat resistance, and good deformation characteristics and corrosion resistance in many aggressive media. The recrystallisation temperature for palladium at 60 – 90 percent deformation is about 400-500\(^\circ\)C [11]. The different phases of the palladium-hydrogen have
been investigated [9, 12-13]. Palladium dissolves large amounts of hydrogen measured by the atomic ratio $n_H = \frac{C_H}{C_{Pd}}$. Palladium, Ti and V metals have high concentrations of hydrogen at low temperature because of a large positive heat of solution, which favours such high hydrogen concentrations. Ni, Fe and Cu metals have low hydrogen concentrations at low temperatures because of a negative heat of solution. The actual hydrogen concentrations in a metal differ from the equilibrium values since the absorption and desorption processes of a hydrogen molecule are usually seriously impeded at the metal surface.

Palladium and its alloys have been widely investigated as a model for a metal-hydrogen system in the view points of thermodynamics and kinetics because of their experimental advantages over other materials in understanding of the mechanism of hydrogen absorption into hydride forming metals [14-18]. High-purity hydrogen is used in many applications, such as an energy source of fuel cells and as a cleaning gas in the manufacture of semiconductors. Pd-Ag alloys are commonly used for hydrogen purification, but the high cost of these membranes significantly limits the field to which they can be applied. In the future, hydrogen selective metal membranes are expected to play a greater role in the production of high purity hydrogen. Palladium-coated V alloy membranes have high hydrogen permeability and are thought to hold promise as replacements for the Pd-Ag alloys [19 – 22].

The Pd-H system has continuously attracted attention, not only because of its technological application in H storage and separation, but also because of
its special place within the more general class of metal hydrides [1, 9, 23 – 25].

Over the years, there has been a continued theoretical interest in the vibrational
energies, the diffusion, and the dissociation of H in pure Pd [26 – 35].
Palladium based alloys are ideal model systems for such investigations because
of their easy servicing and high availability [15]. Theoretical studies of
hydrogen diffusion in alloys with trap sites have considered the effect of the
substitutional – interstitial interaction on this motion [36 – 40].

2.1.2. Infrared spectroscopy concept on diffusion

The infrared spectroscopy shows that the local mode frequencies of
hydrogen in metals lie well above the energy band of host crystal [41] and also
the ratio $M_n \omega_n^2 = M_{n'} \omega_{n'}^2$ is retained. It shows that hydrogen and deuterium
move independently in identical potentials. Whenever the impurity modes lie
above the highest frequency of the perfect lattice, the impurity modes become
localized, the amplitude of vibration of the host lattice atoms in these modes
become very small and it is often a good approximation to assure that only the
impurity atoms move. Indeed neutron diffraction studies on hydrogen in
Vanadium and Niobium [41] have revealed somewhat broadened local modes
with energies of $\hbar \omega_H = k_B x 1000K$ whereas the corresponding energy for $^2H$ is
$\hbar \omega_{^2H} = k_B x 700K$. These energies are considerably higher than Debye energy,
which is in the range $k_B x 200K$ to $k_B x 300 K$ for most metals and $\hbar \omega_H$ and
$\hbar \omega_{^2H}$ are roughly in the ratio expected from the above equation. The Arrhenius
behaviour of diffusion coefficient with temperature can be obtained only above the temperature equivalence of the Debye energy.

Since the diffusion is activated by thermal energy, it is necessary to ascertain the diffusion mechanisms of each isotope of the hydrogen in a given metal as a function of temperature. In the lowest temperature region, where practically less number of phonons is available, hydrogen atoms are expected to migrate by coherent tunneling. As the temperature is raised, process involving a few phonons may take place, and subsequently, those involving many more phonons. These processes are usually called incoherent transitions, in the sense that the coherence of the phonon state is destroyed. When many phonons are available, there is a finite probability that the lattice vibration brings the energy levels of the neighbouring interstitial sites into coincidence to allow transitions of hydrogen atom to occur between these levels. When the perturbation, names as the tunneling matrix element $J$ is small, the transitions occur non-adiabatically with a probability proportional to $J^2$. This process is called thermally activated tunneling. If $J$ is large enough to assure successful jumps, transitions are adiabatic. In many cases, this process seems to take place through some excited state and is realized at relatively higher temperatures. The process is characterized by the fact that the attempt frequency is nearly equal to Debye frequency, independent of isotope mass. At higher temperature, hydrogen atoms can be regarded as classical particles, which execute over-barrier jumps via thermal excitation.
In the high temperature region, hydrogen atoms no longer remain within potential wells of interstitial sites but undergo free motion like the motion of atoms in gases or liquids. This regime will be called 'fluid like diffusion'. The quantum mechanical description is needed to explain the diffusion process in the first two temperature regions. It is instructive to compare the problem of interstitial diffusion with other related mobility problems. The regime of band diffusion is encountered in the electronic conductivity.

In some metal oxides 'small polaron' occurs i.e., electrons which are trapped within a local lattice distortion. They have a mobility which is determined by the thermally activated tunneling process. The theory of small polaron hopping motion has been developed by Holstein [42] to describe the phonon assisted tunneling of electronic carriers in low mobility conductors and insulators. Holstein's non-adiabatic approach to electronic small polaron hopping has been adopted in describing the diffusion of light interstitials in metals [41, 43].

Small polaron transport is concerned with the motion of light diffusing atom between adjacent lattice positions in response to the ever-changing potential associated with the variations of relatively heavy atoms of the lattice. At sufficiently high temperatures, the vibratory motion of the solid becomes classical and the heavy atoms establish positions for which the energy level associated with a light particle occupying a given site momentarily coincides with the energy, if it would have occupied an adjacent site. These temporary
degeneracies, termed coincidence events are each associated with a finite probability of the light particle moving between sites. The applicability of these theories for analysis of experimental results have been severely limited by the lack of realistic estimates of the tunneling matrix elements between neighbouring interstitial configurations.

At low temperature, diffusion data on positive muons in fcc metals Al and Cu were found to exhibit a strong anomaly; the diffusion coefficient becomes nearly independent of temperature. A theoretical interpretation of this anomaly in terms of interaction with conduction electrons has been recently proposed by Kondo [44] and Yamada [45] and a possibility that the same arguments could apply to hydrogen isotopes in Tantalum has been pointed out subsequently by Fukai [46]. The temperature dependence of the diffusion coefficient is not fully known for any solvent, because of experimental difficulties, but several trends are evident. First, both proton’s and deuteron’s jump rates appear to exhibit Arrhenius behaviour

\[ D = D_0 \exp \left( -\frac{E_A}{k_B T} \right) \]

... (2.1)

atleast down to temperature of the order of 150 K. Second, proton diffuse with unusual rapidity. The observed activation energies lie in the range 0.1 to 0.8 eV with the frequency factor from \(4 \times 10^{-4}\) to \(6 \times 10^{-3}\) cm²/sec. Third, large isotope dependence in diffusion rate occur at low temperature in some cases, but in cases studied above room temperature the isotope effect usually appears close to the classical prediction of an inverse-root-mass dependence.
Thus for temperatures above room temperature classical approach can yield good results for diffusion problems.

2.2 THEORETICAL CONSIDERATION ON THE DIFFUSION MECHANISM

In the classical limit the jump frequency of the interstitial hydrogen can be written as

$$\Gamma = \Gamma_0 \exp \left(- \frac{E_a}{k_B T}\right)$$  ... (2.2)

The above equation is valid only when $k_B T > h \gamma_D$ and $k_B T > h \gamma_1$ where $\gamma_D$ is the Debye frequency of the solid and $\gamma_1$ is the localized vibrational mode of the interstitial.

At low temperature region, quantum mechanical description is essential in which adiabatic approximation is used. The essential idea is that the atomic nuclei, being much heavier, move much more slowly than the electrons. As the nuclei move, the electrons follow the nuclear motion adiabatically, in the sense that the electronic state follows a smooth variation merely, as it were, keeping in step, with no abrupt transitions [47].

Details of the approximations involved in [48] may be found in the books by Born and Huang [49] and by Ziman [50]. In this approximation the potential energy of the interstitial is written as a function of the instantaneous position of metal atoms. The interaction between the interstitial and the metal...
atoms confine the interstitial atom within a potential well. The interstitial atom moves from one site to another due to thermal fluctuations.

Whether the transition is adiabatic or not is determined by the tunneling matrix element $J$. If $J > \hbar \gamma_D$ the transition is adiabatic. The jump frequency from site $i$ to $j$ is written as

$$\Gamma = \Gamma_0 \exp \left[ - \frac{(E(B, O) - E(A, O))}{k_B T} \right] \quad \ldots \ (2.3)$$

Where $E(A, O)$ and $E(B, O)$ are the values of the adiabatic potentials at the minimum energy positions and at the saddle point. If $J < \hbar \gamma_D$ the transition is non-adiabatic and the jump frequency becomes

$$\Gamma = \Gamma_0 J^2 \exp \left[ - \frac{(E(B, O) - E(A, O))}{k_B T} \right] \quad \ldots \ (2.4)$$

Where $J$ is treated as a perturbation and $J^2$ is the probability of transition from site $i$ to $j$. This non-adiabatic tunneling is called thermally activated tunneling. It is classified into two (i) Coherent tunneling (Zero Phonon process) and (ii) incoherence tunneling (change in phonon state process).

Schaumann et al [51] pointed out the importance of polaron effects in the diffusion of Hydrogen in metals. Flynn and Stonehaum [41] applied the small polaron theory developed by Holstein [42] for hydrogen diffusion in the non-adiabatic regime. Emin, Baskes and Wilson [43] applied for adiabatic and non-adiabatic regimes. Here $J$ only determines whether the process is adiabatic or not and also involves in the calculation of diffusion constant.

According to Kehr [52] the tunneling matrix element $J$ is
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\[ J = (\frac{\hbar^2}{\pi md} \left[ 8\pi^2 \frac{md^2 V_0}{\hbar^2} \right]^{3/4} \exp \left[ (-2/\pi) \left( \frac{8\pi^2 md^2 V_0}{\hbar^2} \right) \right] ) \] \hspace{1cm} (2.5)

and

\[ \nu_1 = \left( \frac{V_0}{2md^2} \right)^{1/2} \]

Where \( V_0 \) is the potential energy and \( d \) is the distance between two minimas.

From the experimentally measured \( \nu_1 \), \( V_0 \) can be evaluated and hence \( J \). The magnitude of \( J \) obtained is very small.

Sugimoto and Fukai [53] developed a formula for \( J \) in which they consider 2d configuration, in which two neighbouring sites are occupied by interstitial hydrogen atom. The \( J \) value obtained is quite larger.

Flynn and Stoneham [41] developed a quantum diffusion process in the non-adiabatic regime, treating the tunneling matrix element as a perturbation. When \( J \) is assumed to be independent of local lattice distortion (Condon approximation), the jump rate between adjacent sites can be written as

\[ \Gamma = \left( \frac{J^2}{\hbar^2} \right) \int_{-\infty}^{\infty} \phi(t) dt \]

\hspace{1cm} (2.6)

where \( \phi(t) = \exp(-2S(T)) \exp \sum q F_q(t) \) and

\[ S(T) = \sum_q \left( \frac{A_q}{\omega_q} \right)^2 \left( n_q + \frac{1}{2} \right) \]

\hspace{1cm} (2.7)
A_n represents an interaction parameter between a hydrogen atom and a phonon of wave vector q and n_q, the thermal average of the occupation number of the phonons.

\[
F_q(t) = \left(\frac{A_q}{\omega_q}\right)^2 \left[ n_q \exp(i\omega_q t) + (n_q + 1) \exp(-i\omega_q t) \right]
\]  
(2.8)

In the high temperature region \( k_b T \gg h\nu_0 \), the activation type formula given below holds good.

\[
\Gamma = \frac{1}{(J^2/h)(\pi/4E_a k_b T)^2} \exp(-E_a/k_b T)
\]  
(2.9)

Teichler [54] performed more calculations going beyond Condon approximation using the formula.

\[
\Gamma_{ij} = \left(\frac{1}{\hbar}\right) \left(\pi/4E_a k_b T\right)^2 \langle |J_{ij}|^2 \rangle \exp[-(E_j - E_i + 4E_a)^2 / 16E_a k_b T]
\]  
(2.10)

It is noticed that in general the pre-exponential factor of jump rate \( \Gamma_0 \), assumes very different values according to whether the diffusion proceeds via adiabatic or non-adiabatic transition. The pre-exponential factor \( D_0 \) of diffusion constant serves as a useful guide for ascertaining the diffusion mechanism. For H isotopes in fcc, the non-adiabatic transition does not seem to be appropriate for diffusion, as diffusion proceeds via adiabatic transition with activation energy \( E_a \).
The experimental results reveal that it is necessary to take both adiabatic and non-adiabatic transitions in the case of bcc metal. On this basis, Emin et al. [43] derived an expression for jump frequency as

\[
\Gamma = \sum_{ij} \langle r_{ij} p_{ij} \rangle \exp(-E_i / k_B T) / \sum_i \exp(-E_i / k_B T) \tag{2.11}
\]

where \( E_i \) is the energy of the occupied level, \( r_{ij} \) is the probability of occurrence of the coincidence event between the occupied level \( i \) on one site and another unoccupied level \( j \) on an adjacent site and the transfer probability of hydrogen \( p_{ij} \) from \( i \) to \( j \)

\[
p_{ij} = \frac{1 - \exp(-\alpha_{ij})}{1 - \frac{1}{2} \exp(-\alpha_{ij})} \tag{2.12}
\]

where \( \alpha_{ij} = (2\pi / h) |J_{ij}^2 / \varepsilon_{ij}| \), \( \varepsilon_{ij} \) the rate of change of energy difference between the two levels \( i \) and \( j \).

When \( k_B T > h \nu_p \), the diffusion of \(^1\)H interstitial is caused by thermal excitation of the lattice and the diffusion coefficient can be written by the thermal excitation type formula. At low temperature region, it is no longer possible for a system point to surmount the potential barrier of the adiabatic potential surface and the tunneling of the systems point through the potential barrier causing diffusion.

According of Flynn and Stoneham [41], the most important contribution at low temperature comes from the phonon process in which tunneling of the system point occurs by virtual absorption and re-emission of a phonon
conserving the energy of the phonon system. The experiment is not available for the occurrence of two-phonon process.

Teichler and Seeger [55] suggested the theory of one phonon process in diffusion at low temperature. The rate of jump between inequivalent sites and equivalent sites was calculated under the assumption that the energy difference between the initial and final sites of the interstitial \( \Delta E \) is smaller than \( k_B T \).

The jump rate obtained is

\[
\Gamma = \frac{\pi k_B T J_{\text{eff}}^2}{\hbar} (C^0 + \overline{\Delta^2} C^F) \tag{2.13}
\]

where \( \overline{\Delta^2} \) is the second moment of \( \Delta \), so that

\[
\overline{\Delta^2} = \int_{-\infty}^{\infty} (\Delta^2) D(\Delta) d(\Delta) \tag{2.14}
\]

defined in terms of the distribution function of \( \Delta \), \( D(\Delta) \), \( C^0 \) and \( C^F \) are related to the force-dipole, tensor \( p \) of the initial and final state, \( p^i \), and \( p^f \) roughly in the manner

\[
C^0 \propto [\text{tr}(p^i - p^f)]^2
\]
\[
C^F \propto [\text{tr}(p^i + p^f)]^2 \tag{2.15}
\]

The one-phonon process has experimental support [52, 56].

At very low temperatures, diffusion due to phonon assisted tunneling becomes practically impossible and there is a theoretical possibility that a system point, an interstitial surmounted by its phonon clouds, propagates in a small polaron band of width \( J_{\text{eff}} \). This problem has been examined in detail by
Kagan and Klinger [57] and Fujii [58] using the density matrix method. Kondo [44] concluded from his calculation that only in the low temperature region the temperature dependence of the diffusion coefficient is affected by the interaction of conduction electrons with the diffusing atom.

Felter et al. [59] employed the Vibrational Transition State Theory (VTST) to study the surface diffusion. Surface diffusion has been also shown by George et al. [60]. Absolute-rate theory provided a convenient and in fact, customary starting point for a theoretical discussion of solid state diffusion coefficient as

\[ D = f \nu^* e^{\Delta S^* / k_e^{-\Delta H^*/k_B T}} \]  

(2.16)

where \( f \) the correlation coefficient, \( \nu^* \) is the hypothetical vibrational frequency and \( \Delta S^* \) and \( \Delta H^* \) are the entropy and enthalpy of activation.

Varotsos and Alexpoulous [61, 62] have suggested the following relation for single diffusion mechanism:

\[ D(T) = f \alpha^2 \nu \exp\left(\frac{-CB\Omega}{k_B T}\right) \]  

(2.17)

where \( \alpha \) is the edge of the elementary cube, \( \gamma \) the frequency of the diffusing atom for passage through the saddle-point, \( B \) the isothermal bulk modulus, \( \Omega \) the mean volume per atom and \( C \) a dimensionless constant which can be considered as independent of temperature and pressure.
Monte Carlo simulation of hydrogen diffusion in metallic alloys has done by Solomons [63] in which the equilibrium properties of hydrogen in disordered alloys are described by the generalization of multi-site lattice-gas model [64].

Fujita [65] laid down a microscopic foundation of the Arrhenius law for interstitial diffusion with the aid of correlated walk model [66] with the trap possibility. In this approach, the diffusion coefficient $D$ is written as,

$$D = \frac{1}{3} v l q^* \exp(-\frac{\varepsilon}{k_B T})$$  \hspace{1cm} (2.18)

where $v$ is the average migration speed, $l$ is the mean straight path, $q^*$ is a numerical factor of order 1 and $\varepsilon$ is the barrier potential height.

Many authors have studied isotopic effects in the diffusion of hydrogen in metals. The usual starting point for a discussion of isotopic effects in diffusion is the relation of Schoen and of Tharmalingam and Lidiard [67].

$$1 - \frac{D_1}{D_2} = \left[ 1 - \left( \frac{\Gamma_1}{\Gamma_2} \right) \right] f$$  \hspace{1cm} (2.19)

where $\Gamma$ is the diffusion jump frequency and $f$ is a correlation factor.

Ebisuzaki et al. [68] have developed the theory of isotopic effect in the harmonic approximation. They obtained an expression for jump frequency $\Gamma$ by extending the classical transition state theory as discussed in connection with diffusion by Vineyard [69] to account quantum effects. Global mass dependence of the isotopic effect in diffusion has been explained [70] by using
the Short-Memory Augmented Rate Theory (SM-ART) framework of Toller et al. [71]. Quantum mechanical theory of isotopic diffusion in metals has been developed by several authors [72-75].

2.3 EXPERIMENTAL METHODS

In general, hydrogen diffusion is being studied by setting up a non-equilibrium distribution and measuring the time to reach equilibrium under the given conditions. There are also some methods in which hydrogen diffusion in equilibrium is being studied. The available experimental methods of diffusion process are given in Table 2.1.

Table 2.1 The available experimental methods of diffusion process

<table>
<thead>
<tr>
<th>Condition</th>
<th>Method</th>
<th>Information obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-equilibrium</td>
<td>1. Permeation</td>
<td>Diffusivity and Solubility</td>
</tr>
<tr>
<td></td>
<td>2. Elastic After Effect (Gorsky Effect)</td>
<td>Diffusivity.</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>1. Nuclear Magnetic Resonance (NMR)</td>
<td>Jump frequency</td>
</tr>
<tr>
<td></td>
<td>(i) Relaxation time.</td>
<td>Diffusivity</td>
</tr>
<tr>
<td></td>
<td>(ii) Pulsed field gradient</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Quasi-Elastic Neutron Scattering (QNS)</td>
<td>Jump frequency, path &amp; diffusivity</td>
</tr>
<tr>
<td></td>
<td>3. Mossbauer Effect</td>
<td>Isomer shift, Diffusion data</td>
</tr>
<tr>
<td></td>
<td>4. Subscale Micro Hardness Profiling</td>
<td>Diffusivity</td>
</tr>
</tbody>
</table>
2.3.1 Permeation Method

The stationary rate permeation of hydrogen through a metal foil yields only the product of the diffusion coefficient and solubility. Using permeation method, the temperature dependence of diffusion can be accurately determined. In this method the solubility should be measured individually for each sample.

2.3.2 Gorsky Effect

In Gorsky effect method, one measures the elastic after effect that causes due to the application and removal of bending stress. When hydrogen diffuses, the lattice gets expanded and the hydrogen will flow from compression side to tension side of the specimen. On application of stress, an instantaneous elastic deformation is followed by elastic after effect, which continues until the equilibrium distribution for hydrogen atoms is attained. The equilibrium state is such that the diffusion originating from the concentration gradient compensates the flow of H atoms caused by the external stress. The experimentally observed chemical diffusion coefficient $D^*$ of NbH [76] shows that the time constant is very high at low temperatures. This is due to the critical slowing down that takes place as $\partial \mu / \partial \rho$ approaches zero towards the critical temperature of spinodal decomposition of $D^*$ and $\partial \mu / \partial \rho$. The advantage of the Gorsky effect over other methods lie in its insensitivity to surface conditions in addition to its capability of simultaneous determination of
D* and \( \partial \mu / \partial \rho \). The disadvantage is that D* varies with the size of the specimen used.

2.3.3 Nuclear Magnetic Resonance

Since all hydrogen isotopes possess resultant magnetic moments, they are accessible by NMR experiments. NMR measurements are very sensitive to small changes in the metal-hydrogen system under observation. This sensitivity can indeed be an advantage of the technique. A complete knowledge of host-metal structure and phase diagram is essential to analyse the NMR spectrum. Change in electronic structure due to the addition of hydrogen in metals can be determined using NMR. The onset of diffusion of hydrogen has a clear effect on NMR observation. Diffusion constants of hydrogen can be measured directly using NMR with only a very limited knowledge of other properties of the metal-hydrogen system. A brief theory and experimental technique for the determination of hydrogen diffusion parameters from NMR are discussed here.

The activation energy for thermal motion of \(^1\text{H}\) in a metal lattice can be deduced from the knowledge of temperature dependence of mean residence time \( \tau_d \), which is found by the relation,

\[
2\pi(\Delta \gamma) = \left( \frac{\tau_d}{2} \right) \langle \Delta \omega_d^2 \rangle \tag{2.20}
\]

where \( \Delta \gamma \) is the observed line width and \( \langle \Delta \omega_d^2 \rangle \) is the dipolar second moment.
Two different types of experiments are used for the measurement of diffusion coefficients. They are (i) relaxation time measurement and (ii) pulsed field gradient method.

(i) Relaxation Time Measurement

There are three relaxation times namely spin lattice relaxation time $T_1$, the rotating frame spin lattice relaxation time $T_{1\rho}$ and spin-spin relaxation time $T_2$. In NMR, $T_1$ is the longitudinal and $T_2$ is the transverse one. The expressions for the relaxation times due to magnetic dipole-dipole interactions of a single nuclear species are given below [77]:

\[
\frac{1}{T_1} = \frac{3}{2} \gamma_1^2 \hbar^2 I(I+1) \left[ J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right] 
\]  
(2.21)

\[
\frac{1}{T_{1\rho}} = \frac{3}{8} \gamma_1^2 \hbar^2 I(I+1) \left[ J^{(0)}(2\omega_1) + 10 J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right] 
\]  
(2.22)

\[
\frac{1}{T_2} = \frac{3}{8} \gamma_1^2 \hbar^2 I(I+1) \left[ J^{(0)}(0) + 10 J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right] 
\]  
(2.23)

where $\omega_0 = \gamma_1 H_0$ is the Larmor frequency in the static magnetic field $H_0$, $\omega_1 = \gamma_1 H_1$ is the Larmor frequency in the radio frequency magnetic field $H_1$ and $J^{(\rho)}(\omega)$ is the spectral density function which is

\[
J^{(\rho)}(\omega) = \int_{-\infty}^{\infty} G^{(\rho)}(t)e^{-i\omega t} dt 
\]  
(2.24)

where

\[
G^{(\rho)}(t) = \sum_j \langle F^{(\rho)}_j(t') F^{(\rho)}_j(t+t) \rangle 
\]  
(2.25)
with

\[ F^{(p)}_{y}(t) = \frac{d_y Y_{2p}(\Omega_r)}{r_y^3} \]  

(2.26)

\[ d_0^2 = \frac{16\pi}{5}, d_1^2 = \frac{8\pi}{15}, d_2^2 = \frac{32\pi}{15} \]  

(2.27)

\( Y_{2p} \) is the normalized spherical harmonics of order 2p. Diffusion information can be obtained by investigating \( J^{(p)}(\omega) \).

The Bloembergen, Purcell and Pound [BPP] relation formulated by Bloembergen et al. [78] for nuclear relaxation is of the form

\[ G^{(p)}(t) = G^{(p)}(0)\exp(-|t|/\tau) \]  

(2.28)

\[ J^{(p)}(\omega) = G^{(p)}(0)\left(\frac{2\tau}{1 + \omega^2 \tau^2}\right) \]  

(2.29)

and is applied to analyse atomic motion in fluids and further, it has been used extensively for the relaxation in solids as well. The correlation time \( \tau \) of the dipole interaction is related to the mean jump time \( \tau_H \) of diffusing species by \( \tau = \tau_H / 2 \) when the interaction is solely due to interaction between protons whereas \( \tau = \tau_n \) holds for the interaction between protons and metal nuclei.

\( \tau = \tau_0 \exp(-E_a/k_BT) \) used in the BPP formula [78] is found to be in good agreement with the observed \( T_1 \) versus \( 1/T \) curve. There are many cases in which temperature dependence of \( T_1 \) is not reproduced by BPP formula. For these cases, lattice specific models of atomic jumps developed by Fedders and
Sankey [79] and Barton and Sholl [80] are used to reproduce the experimental results using

\[ J^i(\omega) = \left[ \pi d_i^2 / iD \right] \left[ 0.2666 - 0.056(\omega_i^2 / D)^2 + \ldots \right] \]  

(2.30)

(ii) Pulsed Field Gradient Method

In this method, if the spin systems are displaced between 90° and 180° pulses and subject to different values of the magnetic field, the refocusing of the transverse magnetisation is not complete and the signal intensity decreases accordingly. This effect can be used to determine the diffusion coefficient. A pair of field gradient pulses is applied along the direction of the static magnetic field \( H_0 \) before and after the 180° pulse, and the rate of decrease of the spin echo signal is measured as a function of strength and duration of the field gradient pulses. In this technique, one measures the distance along the z-direction of the spin during the time between two successive pulses. Reduction of the spin echo signal is proportional to \( \exp(-D \gamma (\partial H_0/\partial z)^2 t^3 / 12) \) with \( t \approx T_2 \) and \( \partial H / \partial z \leq 100 \) Oe/cm. A comparison of the diffusion coefficient and the mean jump time obtained from the relaxation times allows one to determine the step length of elementary jumps. The pulsed field gradient method provides a unique possibility of observing diffusion of one particular isotope in the presence of other.
2.3.4 Quasi-Elastic Neutron Scattering Studies of Metal Hydrides

Microscopic information about the diffusion process is obtained from Quasi-Elastic Neutron studies. The study of diffusion of an atom in a solid needed a probe, which is sensitive to the motion of the atoms over a distance of a few Angstrom and on a time scale of the order of inverse of the jump frequency of the atom. The technique of quasi-elastic scattering of thermal neutrons offers such a probe. The width of the quasi-elastic peak centered at zero energy transfer is proportional to the jump rate. A major limitation of this technique is that the resolution of the spectrometer is $\tau < 10^{-11}$ s and hence it is difficult to measure the diffusion coefficient at small temperatures. The back scattering technique has been used to study the diffusion of $^1$H in Niobium down to 165 K because $\tau \leq 10^{-9}$ s. Information about the geometry of the interstitial sites over which the diffusing atoms move is obtained from the variation of the width of the quasi-elastic peak with wave vector transfer.

A brief theory for the analysis of neutron scattering results is discussed here by treating the motion of the diffusing atom in the classical limit. The neutron incoherent scattering function $S_{inc}(q,\omega)$ is related to the self-correlation function $G_s(r,t)$ by the equation,

$$S_{inc}(q,\omega) = \frac{1}{2\pi} \int \int G_s(r,t) \exp[i(q\cdot r - \omega t)] dr. dt$$

$$= \frac{1}{2\pi} \int I_s(q,t) \exp(-i\omega t) dt$$

(2.31)
where $\hbar \omega$ and $\hbar q$ are the energy and the momentum transferred in the scattering process. By taking double inverse Fourier transform of the experimental scattering function, $G_s(r,t)$ can be determined. Such a procedure has not been attempted and instead of that the scattering function is calculated from a theoretical model and the parameters of the model can be obtained by fitting to the experimental curves.

Chudley and Elliott [81] proposed a simple model for interstitial diffusion for obtaining scattering function by making use of the following assumptions:

(i) the diffusing atom moves randomly

(ii) the sites over which the particle jumps can form a simple Bravais lattice

(iii) the diffusive jumps are not correlated to the thermal vibration of the particle at equilibrium site and

(iv) all sites are equally available for the diffusing atom.

Including the Debye-Waller factor $\exp[-q^2 \langle u^2 \rangle]$ to account for the form factor due to the vibrational motion of the particle at the equilibrium site, one can get,

$$
S_{ac}^{\text{re}}(q, \omega) = \frac{1}{\pi} \left( e^{-q^2 \omega^2} \right) \frac{f(q)/\tau}{\omega^2 + |f(q)/\tau|^2}
$$

(2.32)

where $f(q)/\tau$ is the width function. The Chudley-Elliott model gives good results for fcc metals, but for bcc metals deviations from experimental results are observed.
Chapter Two

The Mean Square Displacement (MSD) of hydrogen atom can be determined from the slope of intensity versus $q^2$ curve. The intensity of the incoherent scattering is governed by the MSD of the particle due to the thermal motion at the equilibrium site. In the case of Coherent Bragg Scattering, a further contribution to the intensity form factor arises from the local relative displacement of atoms from their regular lattice sites.

Experimental results revealed that with impurities the activation energy is the sum of binding energy due to the impurity and activation energy for diffusion in the undistorted lattice.

2.3.5 Mossbauer Studies

The parameters obtained from Mossbauer spectra of metal-hydrogen systems have yielded information in phase diagrams, magnetic properties, diffusion rates of interstitial hydrogen and changes in the vibrational spectrum ensuing from hydrogenation. In the Mossbauer study, the alloy of the Mossbauer source with host metal is prepared first and then loaded with hydrogen either electrolytically or from the gas phase. The amount of dissolved hydrogen can be determined by the experiment.

2.3.6 Subscale Microhardness Profiling

A novel method of determining hydrogen diffusivity in ductile metallic materials by microhardness profiling the cross-section after cathodic hydrogen charging is given. The first step in the experiment is to suitably load hydrogen
into the material. The use of thick, flat specimens aids data analysis. The most convenient method of loading hydrogen into metallic materials is by electrochemical hydrogen charging. During the charging procedure, care should be taken to maintain reproducible surface conditions and also to eliminate any surface contamination effects. Relatively long charging times lead to distinct microhardness profiles. In order to maintain a constant surface hydrogen concentration throughout the sample surface, it is ideal if the specimen is surrounded on all the sides by the counter electrode (preferably in the form of a wire gauze) during the charging procedure. Otherwise, the sample side that faces away from the counter electrode would have a relatively lower surface hydrogen concentration due to solution resistivity. It would not be possible to completely eliminate the surface layer that forms during cathodic hydrogen charging; however, by choosing an appropriate electrolyte, the thickness of the layer can be kept to a minimum and hydrogen diffusivity through the layer can be conveniently neglected, as a first approximation. Once the material is charged with hydrogen, it has to be immediately cold mounted and the cross-section surface finished (by grinding and polishing) to a condition that is suitable for performing microhardness measurements. The next step is the determination of microhardness profiles across the polished cross-section. The variables in the hardness measurement are the indentation load that is to be used and the distance between successive indentations. Higher indentation loads produce larger indentations and, therefore, the area
that is being sampled is also large in this case [82]. However, larger indentations would result in successive indentations being further apart and, therefore, would not help in gathering more data points. Therefore, lower indentation loads are preferred.

**Analysis of data**

Several microhardness profiles should be generated for each surface of the sample. Averaging over the profiles minimises the measurement errors. Once the microhardness profiles are obtained, it is possible to estimate the diffusivity of hydrogen by making use of the following assumptions: The variation of microhardness (MHv) from surface to bulk is due to the diffusing species (hydrogen). This is reasonable, as generally the variation in microhardness with depth for the uncharged specimens is constant. Assuming \((C - C_b)\) to be proportional to increase in MHv over the bulk value, i.e. \((MHv - MHv_b)\), we obtain,

\[
\frac{C - C_b}{C_s - C_b} = \frac{MHv - MHv_b}{MHv_s - MHv_b}
\]

(2.33)

where \(C_s\) is the surface concentration, \(C_b\) the bulk concentration, and \(C\) the concentration of diffusing species at any point. Subscripts \(b\) and \(s\) denote bulk and surface respectively.

As the specimen surfaces are flat and the depths of diffusion field are small compared to thickness of samples, the problem may be treated as
unsteady diffusion through a semi-infinite flat specimen. Further assumptions that have to be applied to determine the diffusivity is that diffusion occurs through a single phase, there is no internal phase formation in the diffusion field, the diffusion coefficient is constant in the entire diffusion zone, and the surface concentration is not a function of time. It is evident, therefore, that this method cannot be applied to determine diffusivities in materials that are hydrides. However, in such a case, the microhardness profiling technique can be used to monitor the progress of the internal hydriding front, if hydrogen diffusivity is low [83]. Eq. (2.33) can then be combined with the standard diffusion equation to give

\[
\frac{M_{Hv} - M_{Hv_b}}{M_{Hv_s} - M_{Hv_b}} = \frac{C - C_b}{C_s - C_b} = 1 - \text{erf} \left( \frac{z}{\sqrt{4Dt}} \right) = \text{erfc} \left( \frac{z}{\sqrt{4Dt}} \right)
\]

(2.34)

As the assumption of constant surface concentration is not strictly valid because of slight variations in the specimen potential during cathodic hydrogen charging, \(C_s\) should be ideally eliminated from Eq. (2.34). \(C_s\) can be eliminated and the diffusion coefficient can be determined by the following method. A pair of points on the microhardness versus distance curve can be chosen and the following parameter \(Y_{12}\) obtained (for two given points 1 and 2) based on Eq. (2.34) as

\[
Y_{12} = \frac{(C_1 - C_b)/(C_s - C_b)}{(C_2 - C_s)/(C_s - C_b)} = \frac{C_1 - C_b}{C_2 - C_b} = \frac{\text{erfc}(z_1/\sqrt{4Dt})}{\text{erfc}(z_2/\sqrt{4Dt})} = \frac{M_{Hv_1} - M_{Hv_b}}{M_{Hv_2} - M_{Hv_b}}
\]

(2.35)
where \((\text{MHv})_1\), \((\text{MHv})_2\) and \((\text{MHv})_b\) are the microhardness values and \(C_1\), \(C_2\) and \(C_b\) are the hydrogen concentrations at locations 1, 2 and in the bulk, respectively. \(D\) is the only unknown parameter in Eq. (2.35) for a given experiment. Eq. (2.35) can be solved by using error function tables and by trial and error.

The advantage of the microhardness profiling technique is that hydrogen diffusivity can be measured by relatively simple experiments. Moreover, the estimated values are representative of bulk hydrogen diffusion. Of course, the problem with this technique is that it cannot be utilised for materials in which hydrogen diffusivity is relatively fast and also for materials that hydrates or severely crack on introduction of hydrogen. Interestingly, materials that crack on introduction of hydrogen are also not suitable for experimentation in the permeation techniques. In this case, the microhardness profiling technique can be used for a rough determination of diffusivity as the microcracking can be taken into account in the microhardness measurements by choosing an area that is free from cracks for the measurement of microhardness. Another source of error arises if a thick surface layer develops during cathodic charging. This problem can be minimized by choosing a suitable electrolyte that does not produce a thick surface layer during charging.
2.4 OTHER EXPERIMENTAL TECHNIQUES

Felter et al. [59] used a Low-Energy Electron Diffraction (LEED) apparatus to investigate surface diffusion in PdH system. A small electron spot size can be achieved using LEED so that small diffusion path lengths might be probed.

Diffusion of Cr in Ni-Fe alloy was studied experimentally by Cermak [84]. Here the Ni-Fe alloy was prepared by melting the starting materials Ni and Fe in Ar protective atmosphere in an induction furnace. The Ar ion back sputtering chamber is used for microsectioning of the diffusion samples. Cr was deposited by vacuum evaporation onto polished surfaces of the sample. Diffusion anneals were carried out in a vacuum resistance furnace in temperature range from 693 K to 1473 K.

In this case the diffusion is described by

\[ C(x,t) = \text{const.} \exp\left(-\frac{x^2}{4D_{\text{eff}}t}\right) \]  

(2.36)

where \( C(x,t) \) is the mean concentration on depth \( x \) at the diffusion time \( t \). \( D_{\text{eff}} \) is the effective diffusion coefficient defined as,

\[ D_{\text{eff}} = (1 - f)D_v + fD_g \]  

(2.37)

\( D_g \) stands for grain boundary diffusion coefficient, \( D_v \) is the volume diffusion coefficient and \( f \) is the volume fraction of grain boundaries. A good fit of Cr grain boundary diffusion in the NiFe alloy was observed in this method.
Temperature dependence of electrolytic hydrogen diffusion in Nickel was experimentally studied by Namita Mathur and Nigam [85]. In this experiment the Nickel wire samples are subjected to cathodic hydrogen diffusion in a cryostatic bath at lower and higher temperatures.

Cao et al. [86] measured the temperature and azimuthal dependence of the diffusion rates of $^1$H and $^2$H in Ni (111) using a combination of laser-induced absorption and optical diffraction techniques [87]. The experiment was conducted in a conventional ultra high vacuum chamber at an operating pressure less than $5 \times 10^{-12}$ Torr using a Ni disc of 1 cm in diameter. For the diffusion measurement, the first order diffraction of a He-Ne probe laser at $\lambda_p = 0.633 \mu m$ was detected from the adsorbate density grating which is formed by using 10 ns optical pulses from a Nd:YAG laser. The results showed the strong evidence of quantum diffusion of hydrogen in Ni.

The generation of lattice defects and their effects on hydrogen absorption properties described in terms of Pressure-Composition (P-C) isotherms have been investigated as a function of the number of hydrogen absorption cycles for some intermetallic compounds namely, LaNi$_5$ and FeTi [88].

The recovery process of hydrogen dissolved in excess in nickel based alloys was studied by the hydrogen quenching methods and electrical resistance measurements after isochronal and isothermal annealing treatments [89]. A recovery stage of the electrical resistance due to hydrogen in the alloys shows
similar characteristics as observed in resistance decay curves due to H in pure Nickel, e.g., size dependence of the recovery rate and the shape of isothermal recovery curve. Diffusion coefficients of hydrogen are obtained in the range of 240 to 340 K. The values obtained for high temperatures are nearly the same as those for pure nickel, but at low temperatures, especially for the Ni-0.10 at % Cu and Ni-0.10 at % Fe alloys, they are larger than those in pure nickel.

The composition design and processing of hydrogen storage alloys for hydrogen storage and transportation applications have been investigated [90] and the processing improvement, a synthesizing technique based on the Synthesis-Melting-Quenching (SMQ) process, was established which allowed the segregation control and inhibited second-phase transformation, thus avoiding formation of a plateau-slope.

The migration of hydrogen isotopes in pure Pd and Pd-Fe dilute alloys were studied by measuring the electrical resistance at low temperatures [91]. The hydrogen isotopes were charged by heating in a high pressure gas atmosphere or by electrolysis in single crystal plates or polycrystalline wires. The disordered hydrogen isotopes produced by the quenching, migrate to order during annealing. The electrical resistance of the specimen increases due to the ordering and decreases due to the disordering of the hydrogen isotopes. From various isothermal annealing curves for the same specimen, each relaxation time for the resistance increase is determined for various temperatures. The migration energies of hydrogen isotopes are obtained from the above relaxation
times for various concentrations of hydrogen isotopes. The obtained values in pure Pd are nearly the same for single crystal specimen and poly crystalline specimen. The values also do not depend on the hydrogen charging method and also on the hydrogen concentration. The ratio of the diffusion coefficients for hydrogen and deuterium \( \left( \frac{D_{H}}{D_{D}} \right) \) decreases with decreasing temperature. The migration energies of hydrogen isotopes in Pd-Fe dilute alloys are larger than the values for pure Pd. The behaviour of the ratio \( \left( \frac{D_{H}}{D_{D}} \right) \) of the alloys is also the same for that of pure Pd.

The lattice dynamics of hydrogen diffusion for the existence of more than one jump process in palladium-silver alloys [92] and of high-pressure hydrides of the group VI-VIII transition metals [93] have been studied. Investigation of point defect migration by means of fast Doppler broadening technique has been carried out in Fe-Al alloys [94]. The crystal structures, the lattice parameters and the characteristics of hydrogen storage at 303 K have been investigated in the alloys Ti-Cr-V and Ti-Zr-Cr-V [95, 96].

Reported diffusion parameters for hydrogen isotopes in metals Ni, Fe, Ti, Pd, Cu, Ta, Nb, V respectively are given in Tables 2.2 to 2.12 and that in selected alloys are arranged in Table 2.12.

The diffusion constant \( D_0 \) and activation energy \( E_a \) are listed in Table 2.6. From this table, it can be seen that the diffusion coefficient varies depending on the temperature. The diffusion coefficient is also dependent on
the phase structure of palladium as well as differs for different hydrogen isotopes (H, T, D). The diffusion constant \( D_0 \) and activation energy \( E_a \) for palladium alloys are listed in Table 2.7.

**Table 2.2**

The pre-exponential factor \( D_0 \) and the activation energy \( E_a \) for diffusion of hydrogen isotopes in Ni

<table>
<thead>
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<th>Diffusing Element</th>
<th>( D_0 ) in ( \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} )</th>
<th>( E_a ) in meV</th>
<th>Reference</th>
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### Table 2.3

The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Fe

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<th>Diffusing Element</th>
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<th>$E_a$ in meV</th>
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</tr>
<tr>
<td>$^2H$</td>
<td>0.556</td>
<td>063.00</td>
<td>[112]</td>
</tr>
</tbody>
</table>
Table 2.4
The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Ti

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3} \text{ cm}^2 \text{ s}^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>18.00</td>
<td>540</td>
<td>[144]</td>
</tr>
<tr>
<td>H</td>
<td>30.00</td>
<td>640</td>
<td>[145]</td>
</tr>
<tr>
<td>H</td>
<td>-</td>
<td>560</td>
<td>[146]</td>
</tr>
<tr>
<td>H</td>
<td>05.46</td>
<td>553</td>
<td>[147]</td>
</tr>
<tr>
<td>$^2\text{H}$</td>
<td>0.731</td>
<td>1140</td>
<td>[147]</td>
</tr>
</tbody>
</table>
Table 2.5
The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Pd

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$ s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>5.20</td>
<td>244.95</td>
<td>[148]</td>
</tr>
<tr>
<td>H</td>
<td>4.30</td>
<td>242.77</td>
<td>[149]</td>
</tr>
<tr>
<td>H</td>
<td>3.65</td>
<td>242.77</td>
<td>[150]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>2.50</td>
<td>223.28</td>
<td>[150]</td>
</tr>
<tr>
<td>H</td>
<td>4.50</td>
<td>251.47</td>
<td>[151]</td>
</tr>
<tr>
<td>H</td>
<td>4.74</td>
<td>249.29</td>
<td>[152]</td>
</tr>
<tr>
<td>H</td>
<td>5.25</td>
<td>269.72</td>
<td>[153]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>4.46</td>
<td>266.71</td>
<td>[153]</td>
</tr>
<tr>
<td>H</td>
<td>2.94</td>
<td>228.05</td>
<td>[154]</td>
</tr>
<tr>
<td>H</td>
<td>3.95</td>
<td>249.29</td>
<td>[155]</td>
</tr>
<tr>
<td>H</td>
<td>2.50</td>
<td>225.87</td>
<td>[156]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>1.70</td>
<td>205.97</td>
<td>[156]</td>
</tr>
<tr>
<td>$^3$H</td>
<td>10.5</td>
<td>275.31</td>
<td>[157]</td>
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</table>
Table 2.6
Diffusion parameters of Hydrogen isotopes in Palladium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Phase (Pd-H)</th>
<th>T K</th>
<th>$D_0$ $10^{-3}$cm$^2$s$^{-1}$</th>
<th>$E_a$ kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>$\alpha$</td>
<td>230 - 760</td>
<td>2.9</td>
<td>22.2</td>
<td>[158]</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>742 - 1237</td>
<td>2.83</td>
<td>21.7</td>
<td>[159]</td>
</tr>
<tr>
<td></td>
<td>$\alpha + \beta$</td>
<td>293 - 335</td>
<td>1.82</td>
<td>22.2</td>
<td>[160]</td>
</tr>
<tr>
<td></td>
<td>$\beta$</td>
<td>296 - 373</td>
<td>7.76</td>
<td>26.9</td>
<td>[161]</td>
</tr>
<tr>
<td>T</td>
<td>$\alpha$</td>
<td>290 - 322</td>
<td>10.5</td>
<td>26.6</td>
<td>[158]</td>
</tr>
<tr>
<td>D</td>
<td>$\alpha$</td>
<td>218 - 333</td>
<td>1.7</td>
<td>19.9</td>
<td>[158]</td>
</tr>
</tbody>
</table>

Table 2.7
Diffusion parameters of Hydrogen in Palladium alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>T K</th>
<th>$D_0$ $10^{-3}$cm$^2$s$^{-1}$</th>
<th>$E_a$ kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{77}$Ag$</em>{23}$</td>
<td>313 - 473</td>
<td>2.56</td>
<td>21.2</td>
<td>[162]</td>
</tr>
<tr>
<td>Pd$<em>{75}$Ag$</em>{25}$</td>
<td>353 - 673</td>
<td>2.68</td>
<td>21.4</td>
<td>[159]</td>
</tr>
<tr>
<td>Pd$<em>{90}$Ce$</em>{10}$</td>
<td>625 - 1250</td>
<td>1.58</td>
<td>19.3</td>
<td>[163]</td>
</tr>
</tbody>
</table>
Table 2.8
The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Cu

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$ s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>11.50</td>
<td>422.72</td>
<td>[100]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>06.20</td>
<td>391.73</td>
<td>[100]</td>
</tr>
<tr>
<td>H</td>
<td>11.30</td>
<td>402.61</td>
<td>[109]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>07.30</td>
<td>381.73</td>
<td>[109]</td>
</tr>
<tr>
<td>$^3$H</td>
<td>06.12</td>
<td>377.94</td>
<td>[109]</td>
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</tbody>
</table>
Table 2.9

The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Ta

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$ s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.56</td>
<td>1396.16</td>
<td>[164]</td>
</tr>
<tr>
<td>H</td>
<td>75.0</td>
<td>624.43</td>
<td>[165]</td>
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<tr>
<td>H</td>
<td>0.07</td>
<td>119.73</td>
<td>[166]</td>
</tr>
<tr>
<td>H</td>
<td>0.60</td>
<td>151.75</td>
<td>[167]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.33</td>
<td>176.31</td>
<td>[168]</td>
</tr>
<tr>
<td>H</td>
<td>0.65</td>
<td>151.75</td>
<td>[169]</td>
</tr>
<tr>
<td>H</td>
<td>0.44</td>
<td>140.04</td>
<td>[170]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.49</td>
<td>163.05</td>
<td>[170]</td>
</tr>
<tr>
<td>H</td>
<td>0.30</td>
<td>149.58</td>
<td>[171]</td>
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Table 2.10

The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in Nb

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>21.5000</td>
<td>406.23</td>
<td>[172]</td>
</tr>
<tr>
<td>H</td>
<td>56.0000</td>
<td>837.66</td>
<td>[173]</td>
</tr>
<tr>
<td>H</td>
<td>01.6000</td>
<td>179.53</td>
<td>[166]</td>
</tr>
<tr>
<td>H</td>
<td>0.00085</td>
<td>119.72</td>
<td>[174]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.00580</td>
<td>179.45</td>
<td>[174]</td>
</tr>
<tr>
<td>H</td>
<td>0.54000</td>
<td>108.84</td>
<td>[175]</td>
</tr>
<tr>
<td>H</td>
<td>0.50000</td>
<td>105.83</td>
<td>[170]</td>
</tr>
<tr>
<td>H</td>
<td>0.09000</td>
<td>068.11</td>
<td>[170]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.54000</td>
<td>128.74</td>
<td>[170]</td>
</tr>
<tr>
<td>H</td>
<td>18.0000</td>
<td>433.59</td>
<td>[176]</td>
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<td>H</td>
<td>0.00013</td>
<td>055.04</td>
<td>[177]</td>
</tr>
<tr>
<td>H</td>
<td>0.36000</td>
<td>164.82</td>
<td>[177]</td>
</tr>
<tr>
<td>H</td>
<td>1.10000</td>
<td>252.00</td>
<td>[178]</td>
</tr>
<tr>
<td>H</td>
<td>21.5000</td>
<td>410.00</td>
<td>[179]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.52000</td>
<td>127.00</td>
<td>[180]</td>
</tr>
<tr>
<td>H</td>
<td>2.63000</td>
<td>281.00</td>
<td>[147]</td>
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<tr>
<td>$^2$H</td>
<td>4.34000</td>
<td>375.00</td>
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Table 2.11

The pre-exponential factor $D_0$ and the activation energy $E_a$ for diffusion of hydrogen isotopes in V

<table>
<thead>
<tr>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$ s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.44</td>
<td>58.98</td>
<td>[181]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.31</td>
<td>72.87</td>
<td>[181]</td>
</tr>
<tr>
<td>H</td>
<td>0.35</td>
<td>49.86</td>
<td>[170]</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.37</td>
<td>79.82</td>
<td>[170]</td>
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</table>
Table 2.12

Experimental and theoretical diffusion data for some selected alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Diffusing Element</th>
<th>$D_0$ in $10^{-3}$ cm$^2$s$^{-1}$</th>
<th>$E_a$ in meV</th>
<th>Temperature in K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-4.4% V</td>
<td>H</td>
<td>7.100</td>
<td>438.18</td>
<td>-</td>
<td>[104]</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>H</td>
<td>0.018</td>
<td>351.30</td>
<td>283-343</td>
<td>[182]</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>H</td>
<td>0.204</td>
<td>371.04</td>
<td>283-343</td>
<td>[182]</td>
</tr>
<tr>
<td>Fe$<em>{0.5}$Ti$</em>{0.5}$</td>
<td>H</td>
<td>1.010</td>
<td>496.00</td>
<td>380-680</td>
<td>[183]</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.550</td>
<td>481.00</td>
<td>380-680</td>
<td>[183]</td>
</tr>
<tr>
<td></td>
<td>$^2$H</td>
<td>0.820</td>
<td>512.00</td>
<td>400-670</td>
<td>[183]</td>
</tr>
<tr>
<td></td>
<td>$^2$H</td>
<td>0.550</td>
<td>504.00</td>
<td>400-670</td>
<td>[183]</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>1.064</td>
<td>503.30</td>
<td>300-1000</td>
<td>[184]</td>
</tr>
<tr>
<td>Fe$<em>{0.75}$Al$</em>{0.25}$</td>
<td>H</td>
<td>2.872</td>
<td>132.00</td>
<td>850-1000</td>
<td>[185]</td>
</tr>
<tr>
<td>Ni-0.1 at %Fe</td>
<td>H</td>
<td>-</td>
<td>304.08</td>
<td>240-360</td>
<td>[89]</td>
</tr>
<tr>
<td>Ni-1.0 at %Fe</td>
<td>H</td>
<td>-</td>
<td>355.17</td>
<td>240-360</td>
<td>[89]</td>
</tr>
</tbody>
</table>
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