



# Hydrogen concentration estimation in metals at finite temperature using first-principles calculations and vibrational analysis



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## ABSTRACT

In order to clarify hydrogen embrittlement mechanisms and to estimate structural strength of machine components under a hydrogen environment, it is essential to know the hydrogen concentration and its existing state in materials. Solute-hydrogen atoms change the behavior and stability of lattice defects and trigger strength degradation. This paper proposes a method for quantitatively evaluating hydrogen concentrations in metals under various conditions on the basis of first-principles calculations and lattice vibration analysis, to consider the influence of thermal vibrations. First, we give a formulation that yields the hydrogen concentration at interstitial sites and at vacancies and vacancy concentration. We then evaluate the influence of the hydrogen concentration at interstitial sites and sites around vacancies in  $\alpha$ -Fe for the total hydrogen concentration. We show that the influence of the hydrogen around vacancies is small, and that the interstitial hydrogen concentration is the dominant influence when materials are well annealed. We also investigate hydrogen concentrations in various metals (Al, Ni, Cu, Pd, Mo,  $\alpha$ -Ti, Mg, and  $\alpha$ -Zr) and show that the calculated concentrations agree with the experimental data, given that interactions between solute-hydrogen atoms are not significant.

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## 1. Introduction

Hydrogen embrittlement is a well-known phenomenon where solute hydrogen lowers the toughness and ductility of materials. Despite extensive investigations for over a century, the role of hydrogen in materials remains to be fully elucidated. In order to clarify hydrogen embrittlement mechanisms and to estimate structural strength of machine components under a hydrogen environment, it is essential to know the hydrogen concentration and its existing state in materials. Solute-hydrogen atoms change the behavior and stability of lattice defects [1–9] and trigger strength degradation.

Because of environmental problems, it is believed that hydrogen usage under various situations will increase substantially in the near future. Therefore, we need to know the amount of solute hydrogen that dissolves in materials in various usage environments (e.g., high pressure condition and long use at moderate temperature). Although the solute-hydrogen concentration in metals

under hydrogen environments has been measured [10–33], the materials used and temperatures studied are limited. To date, attempts to evaluate total hydrogen content in materials and the existing state of hydrogen in materials have been made by thermal desorption analysis [34–36]. However, the information on trap-site densities in materials (e.g., lattice defect concentration and distribution of inclusions) and knowledge of their hydrogen-trap energy is insufficient, making the existing state of hydrogen uncertain.

An approach based on electronic and atomistic simulations is an effective way to evaluate the hydrogen concentration and distribution in materials under various conditions [37–39]. Using first-principles calculations, the hydrogen-trap energies of lattice defects and inclusions can be calculated [40–43], and using the hydrogen-trap energies and solute-hydrogen concentration obtained via experimentation, hydrogen concentrations around trap sites can be evaluated with the MacLean Formula [42,44,45]. So far, the trap energies have been evaluated at 0 K, and data of solute-hydrogen concentrations in materials have not been sufficiently gathered by the methods mentioned above.

This paper proposes a method for quantitatively evaluating hydrogen concentrations in metals under various conditions on the basis of numerical calculations, and verifies its validity. For our numerical calculations, we use first-principles calculations and perform lattice vibration analysis to consider the influence of temperature, i.e., thermal vibrations.

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It is well known that solute–hydrogen atoms and lattice defects, especially vacancies, have strong interactions [2,3,5,9,46]. Initially, we take into account not only interstitial sites but also trap sites around monovacancies. We then show the influence of hydrogen concentrations at each type of site (i.e., interstitial sites and sites around vacancy) in  $\alpha$ -Fe relative to the total amount of hydrogen. Then, we evaluate hydrogen concentrations in various metals (Al, Ni, Cu, Pd, Mo,  $\alpha$ -Ti, Mg, and  $\alpha$ -Zr), and validate our method by comparing the calculated hydrogen concentrations with experimental data.

## 2. Theory

### 2.1. Gibbs free energy

Here we consider a situation in which hydrogen dissolves in a metal under gaseous hydrogen environment at constant pressure,  $p$ , and temperature,  $T$ . The Gibbs free energy,  $G$ , of the system, where  $n^H$  hydrogen atoms dissolve in metal, is expressed by the following equation:

$$G(p, T, n^H) = E^M + pV^M - TS^M + (N^H - n^H)\mu^H. \quad (1)$$

Here  $E^M$ ,  $V^M$ , and  $S^M$  are the internal energy, volume, and entropy of lattice with  $n^H$  solute–hydrogen atoms, respectively.  $N^H$  is the number of whole hydrogen atoms in the system, and  $\mu^H$  is the chemical potential of each atom of a gaseous hydrogen molecule. We assume that  $E^M$  consists of the ground-state energy of the lattice,  $E_{\text{lat}}$ , and the vibrational energy of the lattice,  $E_{\text{vib}}$ . We also assume that  $S^M$  consists of vibrational entropy,  $S_{\text{vib}}$ , and configurational entropy,  $S_{\text{con}}$ .

We consider a system that has a metallic lattice which includes monovacancies as lattice defects, and hydrogen atoms placed at interstitial sites (both O- and T-sites) and trap sites around the vacancy. Here multiple occurrences of hydrogen trapping are considered around one vacancy. We assume that the interactions between interstitial hydrogen atoms (and between vacancies) can be neglected because of interstitial hydrogen concentration (and vacancy concentration), which is typically very low.

Under this condition,  $G$  can be expressed by the following equation:

$$\begin{aligned} G(p, T, n^{\text{vac}}, n^{\text{vac}+j\text{H},k}, n^{\text{int}+H,l}) &= \left( E_{\text{lat}}^{\text{perf}} + n^{\text{vac}} \Delta e_{\text{lat}}^{\text{vac}} + \sum_j \left( \sum_k n^{\text{vac}+j\text{H},k} \Delta e_{\text{lat}}^{\text{vac}+j\text{H},k} \right) + \sum_l n^{\text{int}+H,l} \Delta e_{\text{lat}}^{\text{int}+H,l} \right) \\ &+ \left( E_{\text{vib}}^{\text{perf}} + n^{\text{vac}} \Delta e_{\text{vib}}^{\text{vac}} + \sum_j \left( \sum_k n^{\text{vac}+j\text{H},k} \Delta e_{\text{vib}}^{\text{vac}+j\text{H},k} \right) + \sum_l n^{\text{int}+H,l} \Delta e_{\text{vib}}^{\text{int}+H,l} \right) \\ &+ p \left( V^{\text{perf}} + n^{\text{vac}} \Delta v^{\text{vac}} + \sum_j \left( \sum_k n^{\text{vac}+j\text{H},k} \Delta v^{\text{vac}+j\text{H},k} \right) + \sum_l n^{\text{int}+H,l} \Delta v^{\text{int}+H,l} \right) \\ &- T \left( S_{\text{vib}}^{\text{perf}} + n^{\text{vac}} \Delta s_{\text{vib}}^{\text{vac}} + \sum_j \left( \sum_k n^{\text{vac}+j\text{H},k} \Delta s_{\text{vib}}^{\text{vac}+j\text{H},k} \right) + \sum_l n^{\text{int}+H,l} \Delta s_{\text{vib}}^{\text{int}+H,l} + S_{\text{con}} \right) \\ &+ \left( N^H - \sum_j \left( \sum_k n^{\text{vac}+j\text{H},k} \right) - \sum_l n^{\text{int}+H,l} \right) \mu^H. \quad (2) \end{aligned}$$

Here superscripts “perf,” “vac,” “vac+ $j$ H, $k$ ,” and “int+ $H$ , $l$ ” indicate perfect crystals without solute–hydrogen atoms, vacancies, vacancies with  $j$  ( $j = 1, 2, \dots, p$ ) hydrogen atoms at the configurational state  $k$  ( $k = 1, 2, \dots, q$ ), and interstitial hydrogen at  $l$  site ( $l = \text{O}$  or  $\text{T}$ ), respectively.  $n^i$  ( $i = \text{vac}, \text{vac}+j\text{H},k, \text{int}+H,l$ ) is the number of “ $i$ .”  $\Delta e_{\text{lat}}^i$ ,  $\Delta e_{\text{vib}}^i$ ,  $\Delta s_{\text{vib}}^i$ , and  $\Delta v^i$  are the changes in ground-state energy, vibrational energy, vibrational entropy, and volume of lattice caused by the formation of “ $i$ ,” respectively. The amount of changes caused by hydrogen dissolution includes the changes in the values of crystal lattice and the values of hydrogen in a metal. Here we treat vacancy concentrations,  $n^{\text{vac}}$ , as a variable parameter in the

formulation. Thus, the change in thermal equilibrium concentration of vacancies, which is caused by trapped hydrogen at a vacancy, is considered.

### 2.2. Chemical potential, $\mu^H$

The partition function  $Z_1$  of a hydrogen molecule is expressed by the following equations [47–49].

$$Z_1 \equiv Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} g_{\text{ele}}, \quad (3)$$

$$\begin{aligned} Z_{\text{trans}} &= \sum_{\text{trans}} \exp\left(-\frac{\epsilon_{\text{trans}}}{k_B T}\right) = \sum_{k_x=1}^{\infty} \sum_{k_y=1}^{\infty} \sum_{k_z=1}^{\infty} \exp\left\{-\frac{h^2}{8ML^2 k_B T} (k_x^2 + k_y^2 + k_z^2)\right\} \\ &\approx \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V, \quad (4) \end{aligned}$$

$$\begin{aligned} Z_{\text{rot}} &= \sum_{\text{rot}} \exp\left(-\frac{\epsilon_{\text{rot}}}{k_B T}\right) = 3 \sum_{l=0,2,4,\dots}^{\infty} (2l+1) \exp\left\{-\frac{\Theta_{\text{rot}}}{T} l(l+1)\right\} \\ &+ \sum_{l=1,3,5,\dots}^{\infty} (2l+1) \exp\left\{-\frac{\Theta_{\text{rot}}}{T} l(l+1)\right\} \\ &\approx \frac{2T}{\Theta_{\text{rot}}}, \quad \left(\Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k_B}\right), \quad (5) \end{aligned}$$

$$\begin{aligned} Z_{\text{vib}} &= \sum_{\text{vib}} \exp\left(-\frac{\epsilon_{\text{vib}}}{k_B T}\right) = \sum_{n=0}^{\infty} \exp\left\{-\frac{\hbar\omega}{k_B T} \left(n + \frac{1}{2}\right)\right\} \\ &= \frac{\exp\left(-\frac{\Theta_{\text{vib}}}{2T}\right)}{1 - \exp\left(-\frac{\Theta_{\text{vib}}}{T}\right)}, \quad \left(\Theta_{\text{vib}} = \frac{\hbar\omega}{k_B}\right). \quad (6) \end{aligned}$$

Here  $g_{\text{ele}}$  is the degeneracy factor of the electron states,  $k_B$  is the Boltzmann constant,  $M$  is the mass of a gaseous hydrogen molecule,  $L$  is the length of side of the cube ( $L^3 = V$ ),  $h$  is Planck's constant,  $I$  is the inertia moment of a gaseous hydrogen molecule,  $\hbar$  is reduced Planck's constant, and  $\omega$  is the angular frequency.  $k_i$  ( $i = x, y, z$ ),  $l$ , and  $n$  are the quantum numbers of translation, rotation, and vibration, respectively.  $\Theta_{\text{rot}}$  and  $\Theta_{\text{vib}}$  in the partition functions of rotation (Eq. (5)) and vibration (Eq. (6)), respectively, are the characteristic temperatures of rotation and vibration, respectively.  $\Theta_{\text{rot}}$  and  $\Theta_{\text{vib}}$  are 85.4 and 6100 K, respectively, for the hydrogen molecule [47,48].  $g_{\text{ele}}$  can be regarded as 1 [47].

The partition function,  $Z_N$ , of  $N$  gaseous hydrogen molecules is given by the following equation, using the partition function  $Z_1$  of one gaseous hydrogen molecule.

$$Z_N = \frac{1}{N!} (Z_1)^N. \quad (7)$$

Thus, the chemical potential,  $\mu^{\text{H}_2}$ , of a gaseous hydrogen molecule is expressed by the following equation.

$$\begin{aligned} \mu^{\text{H}_2} &= \frac{\partial F}{\partial N} = \frac{\partial(-k_B T \ln Z_N)}{\partial N} \approx \frac{\partial}{\partial N} \{-N k_B T (\ln Z_1 - \ln N + 1)\} \\ &= -k_B T \ln \frac{Z_1}{N} \\ &= -k_B T \ln \left\{ \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} \frac{k_B T}{p} \cdot \frac{2T}{\Theta_{\text{rot}}} \cdot \frac{\exp\left(-\frac{\Theta_{\text{vib}}}{2T}\right)}{1 - \exp\left(-\frac{\Theta_{\text{vib}}}{T}\right)} \cdot g_{\text{ele}} \right\}. \quad (8) \end{aligned}$$

In the 1st line, we use the Stirling's formula, and from the 2nd and 3rd line, we use the equation of state of ideal gas,  $pV = Nk_B T$ . Adding the ground-state energy of a gaseous hydrogen molecule,  $e_{\text{H}_2}$ , and

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