

## **Thermodynamics of Gaseous Hydrogen and Hydrogen Transport in Metals**

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### **ABSTRACT**

The thermodynamics and kinetics of hydrogen dissolved in structural metals is often not addressed when assessing phenomena associated with hydrogen-assisted fracture. Understanding the behavior of hydrogen atoms in a metal lattice, however, is important for interpreting materials properties measured in hydrogen environments, and for designing structurally efficient components with extended lifecycles. The assessment of equilibrium hydrogen contents and hydrogen transport in steels is motivated by questions raised in the safety, codes and standards community about mixtures of gases containing hydrogen as well as the effects of stress and hydrogen trapping on the transport of hydrogen in metals. More broadly, these questions are important for enabling a comprehensive understanding of hydrogen-assisted fracture. We start by providing a framework for understanding the thermodynamics of pure gaseous hydrogen and then we extend this to treat mixtures of gases containing hydrogen. An understanding of the thermodynamics of gas mixtures is necessary for analyzing concepts for transitioning to a hydrogen-based economy that incorporate the addition of gaseous hydrogen to existing energy carrier systems such as natural gas distribution. We show that, at equilibrium, a mixture of gases containing hydrogen will increase the fugacity of the hydrogen gas, but that this increase is small for practical systems and will generally be insufficient to substantially impact hydrogen-assisted fracture. Further, the effects of stress and hydrogen trapping on the transport of atomic hydrogen in metals are considered. Tensile stress increases the amount of hydrogen dissolved in a metal and slightly increases hydrogen diffusivity. In some materials, hydrogen trapping has very little impact on hydrogen content and transport, while other materials show orders of magnitude increases of hydrogen content and reductions of hydrogen diffusivity.

### **INTRODUCTION**

Molecular hydrogen adsorbs on metal surfaces and dissociates producing atomic hydrogen, which dissolves into the metal where it interacts with the microstructure and stress fields. If the atomic hydrogen in the metal reaches sufficient levels, it can enhance fracture processes by a number of mechanisms, collectively called hydrogen-assisted fracture or hydrogen embrittlement. In order to understand hydrogen-assisted fracture, it is necessary to understand the concentration and distribution of hydrogen in the metal (thermodynamics) and hydrogen transport in the metal (kinetics). The thermodynamics and kinetics are influenced by a number of factors including the fugacity of hydrogen, surface phenomena, stress fields, and trapping of hydrogen by microstructural features.

We focus on three physical aspects of hydrogen in this brief communication: (1) the real gas behavior of pure gaseous hydrogen and gas mixtures containing hydrogen; (2) the effect of stress on equilibrium hydrogen content and transport in metals; and (3) effects of trapping on hydrogen dissolution and transport in metals. Consider an idealized metallic containment structure for high-pressure hydrogen gas, the fugacity and resulting concentration of hydrogen are high on the inside surface of the metal and essentially zero on the outside surface. At long times, a steady-state concentration profile of hydrogen is achieved across the wall of the structure and hydrogen continuously permeates through the structure; for the purpose of assessing hydrogen content and transport, such a system is referred to as an open system [1]. For the discussion of hydrogen concentration, we focus on thermodynamic equilibrium established between high-pressure hydrogen gas and atomic hydrogen dissolved in the metal on the inside surface of the containment vessel. The equilibrium hydrogen content in a metal depends on the fugacity of hydrogen in contact with the metal surface. A framework for quantifying the fugacity of high-pressure hydrogen is presented and extended to gaseous mixtures containing hydrogen. The fugacity of hydrogen affects the transport of hydrogen in the metal, as described by fundamental transport equations; however, it is assumed that the transport parameters, namely the hydrogen diffusivity, are independent of hydrogen concentration (in the absence of stress and trapping), thus independent of hydrogen fugacity.

Stress and hydrogen trapping affect the equilibrium concentration of hydrogen in the metal as well. In addition, the effective hydrogen diffusivity in the metal can be influenced by both factors. We briefly summarize the magnitude of these effects for both hydrogen concentration and hydrogen diffusivity. While the effect of stress is relatively straight forward, hydrogen trapping depends on several parameters, resulting in a wide range of possibilities. To illustrate the spectrum of hydrogen trapping in metals, two examples are briefly considered: (1) in iron, representing ferritic steels, hydrogen trapping can substantially impact hydrogen concentration and transport and (2) in austenitic stainless steel ( $\gamma$ -SS), the effects of hydrogen trapping are relatively small.

A general understanding of the real gas behavior of hydrogen, effects of stress and hydrogen trapping provide a basic framework for assessing the hydrogen concentration and distribution of hydrogen in metals in the absence of surface phenomena. These effects, however, can be highly localized in real structures and comprehensive modeling is necessary to evaluate interactions between hydrogen and the mechanics of flaws and defects in real structures. In a number of important manuscripts [2-5], Sofronis and colleagues have integrated the thermodynamics and transport equations into comprehensive mechanics-based models and applied these models to engineering structures [4].

## **THEORY**

### **Hydrogen Solubility**

For understanding and quantifying hydrogen-assisted fracture in structural metals for containment of gaseous hydrogen, it is necessary to quantify the amount and distribution of hydrogen dissolved in the metal. At the surface of a metal, equilibrium is established between the diatomic hydrogen molecule and hydrogen atoms dissolved in the metal lattice:



This equilibrium condition is defined by the equivalence of the chemical potential of hydrogen in the gas phase ( $\mu_{HH}$ ) and in the metal ( $\mu_H$ ), which in the absence of stress can be expressed as

$$\frac{1}{2} [\mu_{HH}^o + RT \ln(f_{HH} / f_{HH}^o)] = \mu_H^o + RT \ln a_H \quad (2)$$

where  $R$  is the universal gas constant,  $T$  is the temperature in Kelvin,  $f$  is the fugacity of the gas (which is equivalent to the pressure in the case of an ideal gas), and  $a$  is the activity of hydrogen in the metal, while the superscript  $o$  refers to the standard state and the subscripts  $HH$  and  $H$  refer to the diatomic gas and hydrogen dissolved in the metal respectively. In structural metals, the concentration of hydrogen in equilibrium with the gas phase is very low, and the standard state is defined such that  $a_H = c_o$  (where  $c_o$  is the moles of hydrogen per moles of metal atoms in the absence of stress, which is approximately equal to the molar fraction of hydrogen). Equation 2 is the theoretical origin of Sievert's Law:

$$K = \frac{c_o}{f^{1/2}} \quad (3)$$

where  $K$  is the equilibrium coefficient for the reaction expressed in equation 1, also called the hydrogen solubility in this context. Furthermore, recognizing that  $K$  is related to the free energy of the reaction, the hydrogen solubility can be expressed in terms of its temperature dependence:

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) \approx K_o \exp\left(\frac{-\Delta H^o}{RT}\right) \quad (4)$$

where  $\Delta G^o$  and  $\Delta H^o$  are the standard free energy and enthalpy of the reaction in equation 1 and  $K_o$  is a constant (related to the entropy term). The solubility of hydrogen in metals is typically reported in terms of equation 4 (Table 1), and the equilibrium lattice concentration of hydrogen in a metal exposed to gaseous hydrogen can be determined from equation 3.

### **Fugacity of gases**

As noted above, to predict the amount of lattice hydrogen dissolved in a metal from a gas, we need to know the fugacity of the hydrogen gas. This requires knowledge of the equation of state (EOS) for gaseous hydrogen, which for ideal gases is simply the ideal gas law:  $V_m = RT/P$ , where  $V_m$  is the molar volume of the gas and  $P$  is the gas pressure. The ideal gas law, however, does a poor job of predicting the state of the gas at high pressure. Numerous complicated, often transcendental, equations have been developed to describe the real behavior of gases over a wide range of pressure and temperature [6, 7]. On the other hand, for common engineering conditions, a simple one-parameter EOS provides an accurate prediction of the real gas behavior of hydrogen (and many other gases) [8]. This Abel-Noble EOS has the form

$$V_m = \frac{RT}{P} + b \quad (5)$$

where  $b$  is the co-volume constant, which can be thought of as the volume of the molecules. The Abel-Noble relationship provides accurate predictions of the state of some gases for conditions where the volume of the ideal gas ( $RT/P$ ) is larger than  $b$ . For hydrogen, a single value of  $b = 15.84 \text{ cm}^3/\text{mol}$  describes the real gas behavior for conditions appropriate to engineering components for hydrogen storage applications:  $T > 223 \text{ K}$  and  $P < 200 \text{ MPa}$  [9].

For determining lattice hydrogen concentrations (equation 3), we require knowledge of the fugacity of the gas. The fugacity can be derived from the Abel-Noble EOS [9] and can be expressed as a ratio with respect to pressure (sometimes referred to as the fugacity coefficient):

$$\frac{f}{P} = \exp\left(\frac{P}{RT}b\right) \quad (6)$$

It should be clear from equation 6 that, as  $P$  decreases and  $T$  increases, the exponential term goes toward a value of one and  $f \rightarrow P$  as expected for gases that tend toward ideal behavior. For systems that contain an ideal mixture of gases, the Lewis-Randall rule states that the fugacity of the  $i$ -th component ( $f_i$ ) of the gas is dependent on its molar fraction ( $x_i$ ) and the fugacity of that component at the total pressure ( $f$ ), similar to the relationship for partial pressure:

$$f_i = x_i f \quad (7)$$

The assumption of an ideal mixture should not be confused with ideal gas behavior: a gas mixture is ideal if each component can be described independently of the other components, which should be a reasonable assumption for gases in the range of applicability of the Abel-Noble EOS (since it is assumed by the Abel-Noble EOS that the gas molecules do not interact). The mole fraction of the  $i$ -th component can be determined from the EOS and the sum of partial pressures as

$$x_i = \frac{p_i/Z_i}{\sum_j (p_j/Z_j)} \quad (8)$$

where  $p_i$  is the partial pressure of the  $i$ -th component and  $Z_i$  is the compressibility, which for the Abel-Noble EOS is given by  $Z_i = 1 + (p_i/RT)b_i$ . Combining equations 6 and 7 for a system containing a mixture of gases with hydrogen partial pressure of  $p_{HH}$ , the ratio of the fugacity of hydrogen to the partial pressure of hydrogen is

$$\frac{f_{HH}}{p_{HH}} = \frac{x_{HH}P}{p_{HH}} \exp\left(\frac{P}{RT}b\right) \quad (9)$$

Since the term  $x_{HH}P/p_{HH}$  is approximately equal to (or greater than) one, and  $P \geq p_{HH}$ , the fugacity of hydrogen in a gas mixture (equation 9) will be equal to or greater than the fugacity of pure hydrogen (equation 6) at  $p_{HH}$ :  $f_{HH} \geq f$ , where both are evaluated at  $p_{HH}$  ( $f$  is fugacity of pure hydrogen).

## **Effect of Stress**

Stress affects the lattice spacing in crystalline solids, which affects both the amount of hydrogen that can dissolve and the diffusion of hydrogen in the stressed lattice. Stress, then, affects both the thermodynamics and kinetics of hydrogen in metals, both of which should be addressed to quantify the effect of stress on hydrogen in the metal.

The concentration of hydrogen dissolved in a metal lattice under stress ( $c_L$ ) can be determined from the fundamental principles of thermodynamics. Generally, this is expressed as [10, 11]

$$\frac{c_L}{c_o} = \exp\left(\frac{\sigma V_H}{RT}\right) \quad (10)$$

where  $\sigma$  is the equivalent local hydrostatic stress (one-third the sum of principal stresses), and  $V_H$  is the partial molar volume of hydrogen (which for iron and steel is about 2 cm<sup>3</sup>/mol [1, 11], Table 1). From this relationship, it should be clear that when the stress is positive (tensile) the concentration of hydrogen is increased ( $c_L/c_o > 1$ ); while when the stress is negative (compressive), the concentration is decreased ( $c_L/c_o < 1$ ).

The kinetics of hydrogen transport under an applied stress have been modeled by Sofronis using solid mechanics and linearizing solutions to the fundamental transport equations [12]. He found that, assuming a dilute solution, the effective diffusivity in a metal under stress ( $D_s$ ) can be related to the diffusivity in a stress-free lattice ( $D$ ) by

$$\frac{D_s}{D} = 1 + \frac{c_o}{V_M} \left[ \frac{2}{9} \frac{E}{(1-\nu)} \frac{V_H^2}{RT} \right] \quad (11)$$

where  $E$  and  $\nu$  are the material's Young's modulus and Poisson's ratio, respectively, and  $V_M$  is the molar volume of the metal (not to be confused with  $V_m$  the molar volume of the gas). Interestingly, this relationship is independent of the magnitude of the stress, but depends linearly on  $c_o$ , the concentration of hydrogen in the *stress-free* state.

## **Effect of Trapping**

Hydrogen, being generally mobile, interacts with various features of a microstructure and can be trapped by many of these features. Hydrogen traps are characterized by the energy that binds the hydrogen to the trap site ( $W_B$ ), which can be described by a simple thermodynamic equilibrium outlined by Oriani [13]:

$$\frac{\theta_T}{1 - \theta_T} = \frac{\theta_L}{1 - \theta_L} \exp\left(\frac{W_B}{RT}\right) \quad (12)$$

where  $\theta_L$  is the fraction of hydrogen lattice sites that are occupied and  $\theta_T$  is the fraction of filled hydrogen traps. These fractions are related to the concentration of lattice hydrogen ( $c_L$ ) and the concentration of trapped hydrogen ( $c_T$ ) by

$$\theta_L = c_L / \beta n_L \quad (13)$$

$$\theta_T = c_T / \alpha n_T \quad (14)$$

where  $\beta$  is the number of hydrogen lattice sites per metal atom,  $n_L$  is the concentration of metal atoms,  $\alpha$  is the number of hydrogen trapping sites per trap, and  $n_T$  is the concentration of hydrogen traps. We assume that both  $\alpha = 1$  and  $\beta = 1$ , as commonly assumed in the literature [4], although theoretically this depends on the character of the trap sites and lattice crystal structure. In structural metals, the fraction of lattice sites occupied by hydrogen is small, thus  $\theta_L \ll 1$ . Substituting equations 13 and 14 into equation 12, we arrive at an expression for the concentration of trapped hydrogen in terms of  $c_L$ ,  $n_L$ ,  $n_T$ , and  $W_B$  [2]:

$$\frac{c_T}{c_L} = \frac{(n_T/n_L)}{\left[ \frac{c_L}{n_L} + \exp\left(\frac{-W_B}{RT}\right) \right]} \quad (15)$$

It is generally postulated that when trapping is operative an effective diffusivity ( $D_{eff}$ ) can be identified that follows the same phenomenological form as Fick's first law. Thus,  $D_{eff}$  can be expressed in terms of the true lattice diffusivity  $D$  and the relationship between trapped and lattice hydrogen [13]:

$$\frac{D_{eff}}{D} = \frac{1}{1 + \partial c_T / \partial c_L} = \frac{1}{1 + \frac{c_T}{c_L} (1 - \theta_T)} \quad (16)$$

The quantities in equations 15 and 16 are generally expressed in terms of atoms or atomic sites per unit volume, where for example the number of atoms per unit volume  $N_L$  is equivalent to  $n_L N_A / V_M$  (and  $N_A$  is Avogadro's number for the definition of a mole). In the present analysis, we use moles of hydrogen per mole of metal (expressed as H/M) and moles of traps per mole of metal. This formulation has the advantage that the volume and number of atoms are eliminated in favor of simple mole ratios, such that  $n_L = 1$ .

## DISCUSSION

### Equilibrium Hydrogen Concentration

For a pure gas, the ratio of the fugacity to the pressure of hydrogen is an exponential function of the pressure (equation 6). The ratio  $f/P$  can be greater than 2 at high pressure ( $> 100$  MPa) for ambient temperature and is greater at lower temperature, but  $f/P < 1.1$  for  $P < 15$  MPa ( $\sim 2200$  psi, i.e., approximate maximum pressure of industrial gas cylinders). The concentration of hydrogen in the metal that is in equilibrium with the gas ( $c_o$ ) is related to the square root of fugacity (equation 3); consequently, in general,  $c_o$  is not strongly dependent on fugacity. The increase in  $c_o$  due to real gas behavior, for example, is relatively small compared to the effects of temperature on hydrogen solubility (equation 4). At hydrogen pressure of 15 MPa,

the  $c_o$  determined from equation 3 using the real gas behavior is greater than predicted for the ideal gas by 5%.

As a simple example of gas mixtures, consider a system of helium and hydrogen at room temperature, assuming real gas behavior of both gases ( $b_{He} = 10 \text{ cm}^3/\text{mol}$  [8]). For a gas mixture with  $P = 15 \text{ MPa}$ ,  $f_{HH}/p_{HH}$  is largest when the  $p_{HH}$  is lowest and converges to the value for the pure hydrogen state as  $p_{HH}$  approaches  $P$  (Figure 1). For a hydrogen-helium mixture at pressure of 15 MPa with hydrogen partial pressure of 5 MPa,  $f_{HH}/p_{HH} = 1.11$ . The value of  $c_o$  for this gas mixture is increased by slightly greater than 5% compared to the value predicted for the ideal hydrogen gas at 5 MPa (ignoring the role of stress). Curves similar to that presented in Figure 1 can be developed for other values of  $P$  and other gases (with appropriate EOS). Consider, for example, a high-pressure system of hydrogen and helium with  $P = 100 \text{ MPa}$ ,  $f_{HH}/p_{HH} > 2.5$  for  $p_{HH} = 5 \text{ MPa}$  and  $f_{HH}/p_{HH} > 2$  for  $p_{HH} = 30 \text{ MPa}$ . In general, an increase in fugacity due to the presence of the other gases is modest unless the total pressure  $P$  is large compared to the partial pressure of hydrogen  $p_{HH}$ .

If the gases react, the pressure and fugacity of hydrogen can be substantially reduced (or increased if hydrogen is being generated). Mixtures of hydrogen and deuterium represent a simple example, where the formation of the HD molecule lowers the partial pressure of both  $\text{H}_2$  and  $\text{D}_2$  [14]. In this case, due to reduced partial pressure, the concentration of dissolved isotopes is less than might be expected based on a system of  $\text{H}_2$  and  $\text{D}_2$  only.

Residual and applied stresses can contribute substantially to changes in equilibrium hydrogen content (Figure 2). The role of stress on hydrogen concentration is particularly important at crack tips, where the local tensile stresses can be high compared to the applied stress, and near welds, where residual tensile stresses can be high. The equilibrium lattice hydrogen contents in these areas will be higher than in the stress-free state, which enhances the susceptibility of these regions to hydrogen-assisted fracture. Since the hydrogen content depends on the local equivalent hydrostatic stress, high-strength materials will tend to have higher hydrogen contents due to the greater tensile stresses that are generally applied to these materials. Sofronis and collaborators have modeled hydrogen transport and the enhanced hydrogen content at defects in steels [2-4] and superalloys [5].

In the case of compressive stresses, the hydrogen content is lowered (Figure 2). Processes that develop compressive residual stresses on the surface of components (such as shot-peening or laser-peening) can thus reduce the surface concentrations of atomic hydrogen. Moreover, compressive stress can reduce crack initiation and crack propagation compared to the absence of these compressive residual stresses [15]. The combination of these two observations provides some optimism that surface compressive stresses may extend lifetimes of components that fail due to hydrogen-assisted crack initiation at surfaces.

Hydrogen trapping can also increase the equilibrium hydrogen content in a metal and its impact can be substantially larger than the contributions of real gas behavior or tensile stresses. The amount of trapped hydrogen depends strongly on the energy associated with the trap ( $W_B$ ) and the density of traps ( $n_T$ ), as well as the available lattice hydrogen; Hirth discusses in some detail the microstructural features that trap hydrogen in iron [1]. In Figure 3, we compare  $c_T/c_L$  for two binding energies:  $W_B$  equal to 20 and 60 kJ/mol. The lattice concentration was chosen to be consistent with the equilibrium lattice concentration of iron at hydrogen pressure of 15 MPa based on solubility data reported in Kumnick and Johnson [16]:  $c_L = 10^{-7} \text{ H/M}$  (moles of H atoms per mole of metal). The higher energy trap is characteristic of iron [1, 16] and shows that trapping can account for the majority of hydrogen in the metal if the density of trapping sites is

sufficiently high. The lower trap energy is characteristic of austenitic stainless steels [17] resulting in  $\theta_T \ll 1$ . Low-energy hydrogen traps, thus, have little impact on hydrogen content except at very high  $n_T$  (Figure 3). Experimental data show  $c_L$  to be three to four orders of magnitude greater for the austenitic stainless steels compared to iron and steels [18]. A higher value of  $c_L = 10^{-3}$  H/M reduces  $c_T/c_L$  while necessarily increasing the total hydrogen content (Figure 4) for both high and low energy traps. In general, hydrogen trapping has the largest effect on total hydrogen contents when the binding energy of the traps is high (iron), the lattice concentration is low (iron), and the concentration of hydrogen traps is high (e.g., as may be the case in some high-strength microstructures).

## **Hydrogen Transport**

The idea that stresses can change the rate of diffusion is easy to conceptualize: dilation of the lattice due to stress should influence the probability that a mobile species will “hop” from one site to the next. As described above, thermodynamic models predict that the effective hydrogen diffusivity is enhanced in a stress field, but this change is not directly dependent on stress and linearly dependent on  $c_o$  (equation 11) [12]. The magnitude of this change, however, is relatively modest. The diffusivity of hydrogen in a stress field relative to the lattice diffusivity of hydrogen  $D/D$  is plotted in Figure 5 and shows that for low  $c_o$  (for iron  $c_o \ll 10^{-4}$  H/M) the diffusivity is unaffected by stress. For alloys with high solubility such as stainless steels [9], however, the increase of diffusivity in high-pressure hydrogen gas could be around 5% at room temperature ( $c_o \sim 0.003$  H/M for  $\gamma$ -SS in 140 MPa hydrogen), and perhaps as high as 8% at elevated temperature ( $c_o \sim 0.01$  H/M at 573 K). These are relatively small changes considering that the hydrogen diffusivity can range by an order of magnitude for modest changes of temperature ( $\Delta T \sim 30$  K).

Measurements of hydrogen diffusivity in steels subjected to an elastic strain have shown little change in hydrogen diffusivity [11, 19, 20], consistent with the analysis above. Plastic strains, on the other hand, generate additional hydrogen traps, thus deformation affects hydrogen trapping and hydrogen transport [4, 5, 16]. As shown by equation 16, trapping of hydrogen will invariably reduce the effective diffusivity ( $D_{eff}$ ) compared to the lattice diffusivity ( $D$ ). In the limit that trap sites are unfilled ( $\theta_T \ll 1$ ),  $D_{eff}/D$  will depend on hydrogen concentration:  $D_{eff}/D = c_L/(c_T + c_L)$ . In materials where  $W_B$  and  $n_T$  are relatively large,  $D_{eff}$  can be several orders of magnitude less than  $D$  in this limit. However, such a condition is only encountered as a transient condition (e.g., initially upon hydrogen exposure). For example in iron, reported values of hydrogen diffusivity range over several orders of magnitude at low temperature, but consistent values are measured at elevated temperature [21]; trapping provides an explanation for these observations. At elevated temperature, the dependence of  $D_{eff}$  on hydrogen concentration is eliminated because hydrogen trapping is essentially deactivated as shown by the condition  $\theta_T \approx 0$  and  $c_L \gg c_T$  (Figure 6). Measurements of diffusivity at elevated temperature then are approximately the lattice diffusivity  $D$ , which is generally presumed to be independent of hydrogen content. With lattice diffusivity carefully measured at elevated temperature and knowledge of the trapping characteristics of the material,  $D_{eff}$  can be determined and used in transient calculations as demonstrated by Sofronis and colleagues [2-5], while measurements at low temperature have limited value.



## SUMMARY

In summary, the thermodynamics and kinetics of hydrogen dissolution and transport in metals are influenced by several physical characteristics: hydrogen fugacity, residual and applied stresses, and hydrogen trapping. In the limit of ideal gas behavior, the hydrogen fugacity is the pressure. At high pressure and low temperature the fugacity can differ from the pressure by more than a factor of 2. Equilibrium concentrations of hydrogen are proportional to the square root of the fugacity, therefore real hydrogen content is greater than predicted by an ideal-gas analysis by substantially less than a factor of 2. The effects of residual and applied stresses on dissolved hydrogen contents are of similar, modest magnitude. Stress also increases diffusivity; however, the magnitude of this increase is small except in materials with very high hydrogen solubility (and independent of the magnitude of the stress). Hydrogen trapping can have a much larger impact on the thermodynamics and kinetics of hydrogen in metals in some materials, depending on the characteristics of the traps. In iron, and by extrapolation in ferritic steels, hydrogen trapping near ambient temperature significantly increases hydrogen content in the steel and substantially reduces the effective hydrogen diffusivity under transient conditions. At elevated temperature ( $>600$  K), hydrogen traps are essentially inactive. Hydrogen trapping in austenitic stainless steels is predicted to have little effect on hydrogen concentration and hydrogen diffusivity. These basic thermodynamic and kinetic characteristics are important for understanding hydrogen-assisted fracture in steels and for interpreting experimental data. Engineering models can and are using these physics to clarify the transport of hydrogen during the fracture process and are necessary for predictive simulation in real systems.

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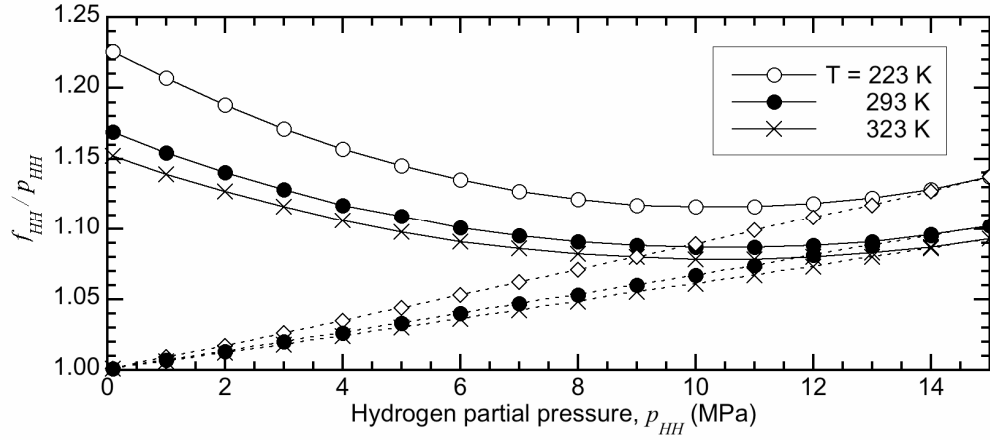
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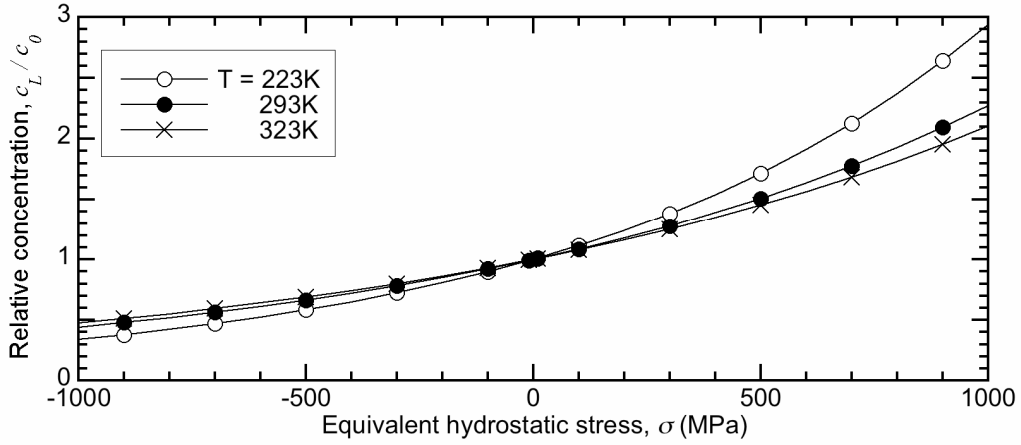
**Table 1.** Material properties and parameters used in calculations.

Property	Units <sup>†</sup>	Value	Reference
Hydrogen Gas			
$b$	cm <sup>3</sup> /mol	15.84	[9]
Metal			
$V_M$	cm <sup>3</sup> /mol	7.1	—
$E$	GPa	200	—
$\nu$	—	0.33	—
Hydrogen in iron and steel			
$V_H$	cm <sup>3</sup> /mol	2	[1, 11]
Hydrogen in iron			
$W_B$	kJ/mol	60	[16]
$K_o$	H/M MPa <sup>-1/2</sup>	0.00171	
$\Delta H^o$	kJ/mol	27.2	
Hydrogen in austenitic stainless steel ( $\gamma$ -SS)			
$W_B$	kJ/mol	20	[17]
$K_o$	H/M MPa <sup>-1/2</sup>	0.00192	[9]
$\Delta H^o$	kJ/mol	5.9	

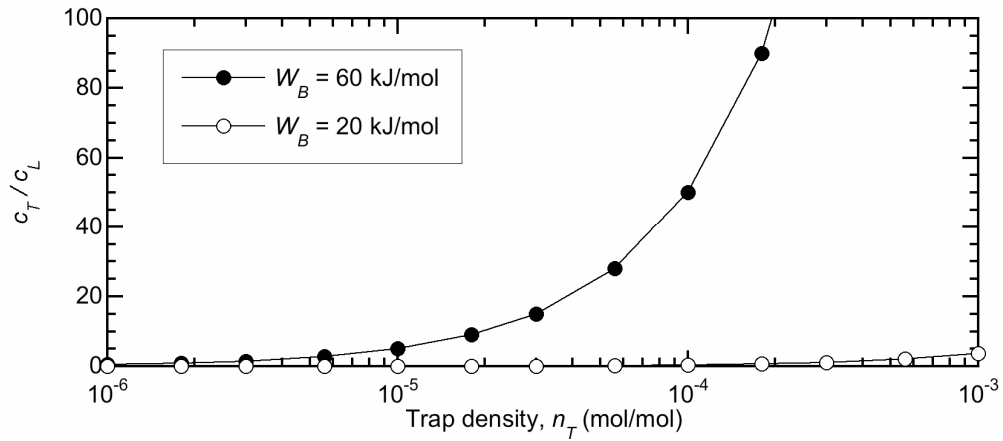
<sup>†</sup> H/M = moles of H atoms per mole of metal atoms



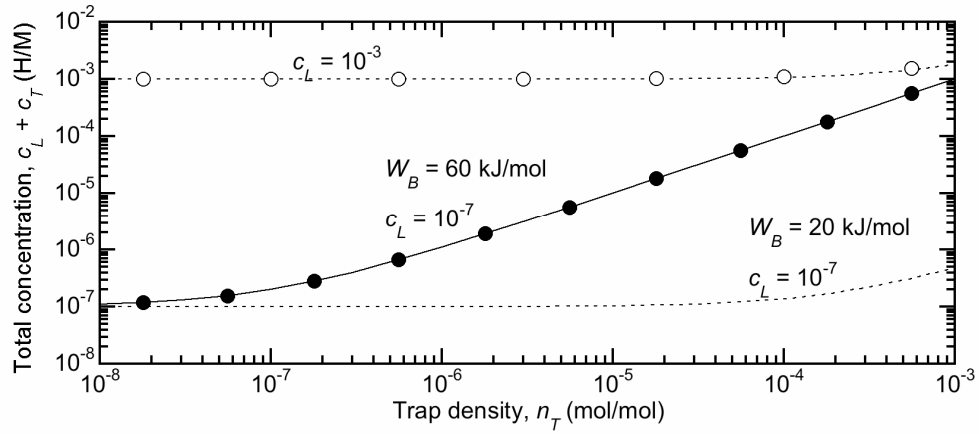
**Figure 1.** Ratio of hydrogen fugacity to hydrogen partial pressure as a function of hydrogen partial pressure for a hydrogen-helium system at  $P = 15$  MPa; the dotted lines represent the pure hydrogen case.



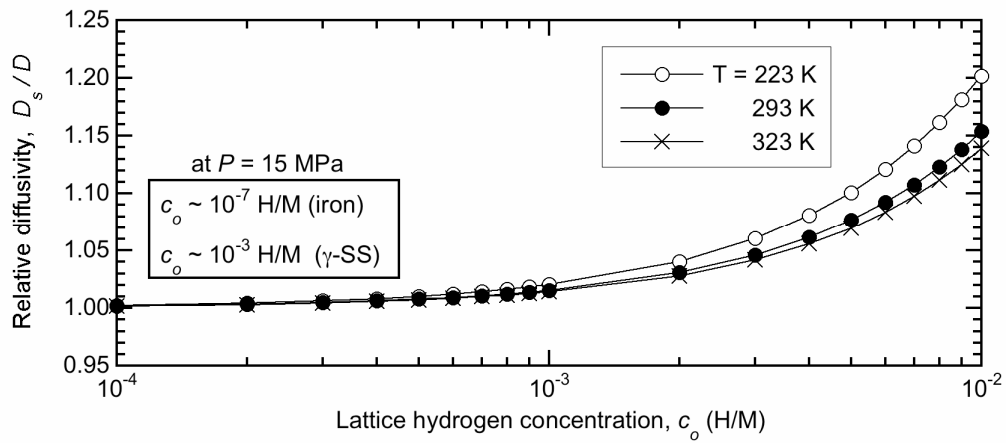
**Figure 2.** Relative concentration of hydrogen as a function of equivalent hydrostatic stress.



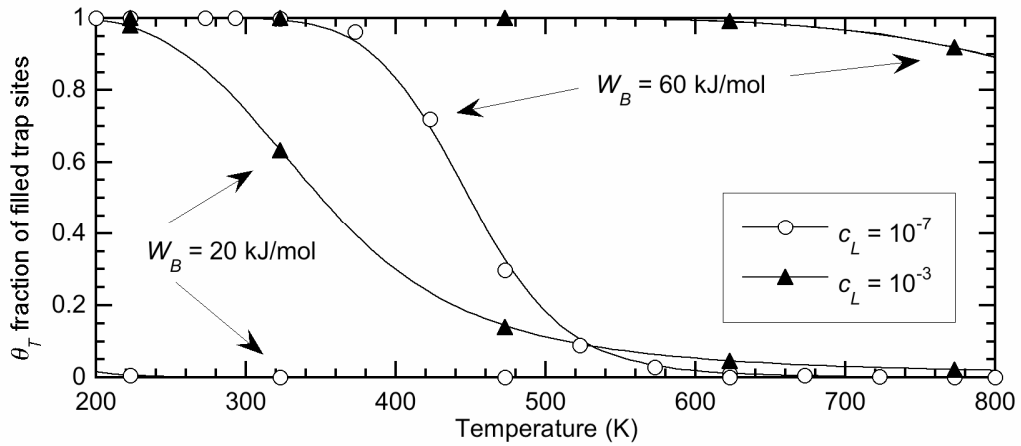
**Figure 3.** The concentration of trapped hydrogen ( $c_T$ ) relative to lattice hydrogen ( $c_L = 10^{-7}$  H/M) as a function of the density of trap sites ( $n_T$ ) at 293 K.



**Figure 4.** The total concentration of hydrogen as a function of the density of trap sites ( $n_T$ ) at 293 K. The curves for the two binding energies ( $W_B$ ) with  $c_L = 10^{-3}$  are essentially indistinguishable.



**Figure 5.** The effective diffusivity due to stress relative to the lattice (stress-free) diffusivity ( $D_s/D$ ) as a function of lattice hydrogen concentration.



**Figure 6.** The fraction of filled traps as a function of temperature.