SAND2008-1760C

MRS Spring 2008 Meeting, session HH: "The Hydrogen Economy"

Thermodynamics of Gaseous Hydrogen and Hydrogen Transport in Metals

C. San Marchi and B.P. Somerday
Sandia National Laboratories, 7011 East Ave, Livermore 94550

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 interactions 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, but more broadly is important for enabling a comprehensive understanding of hydrogen-assisted fracture. We start by providing a framework for understanding the thermodynamics of gaseous hydrogen in real gas systems and extend the pure gas system to 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. Equilibrium analysis shows that a mixture of other gases in hydrogen will increase the fugacity of the hydrogen gas, but the increase in hydrogen fugacity is small for practical systems and will generally be insufficient to substantially impact hydrogen-assisted fracture. Analysis of the gas phase is followed by the consideration of the effects of stress and hydrogen trapping on the transport of atomic hydrogen in metals. Stress and trapping can both increase the amount of hydrogen dissolved in a metal. Hydrogen diffusivity is increased by stress and can be substantially reduced by trapping.

INTRODUCTION

Hydrogen-assisted fracture is a process where hydrogen dissolves into a material interacting with the microstructure and stress fields to enhance fracture processes. In order to understand these processes, it is necessary to understand the concentration and distribution of hydrogen in the metal (thermodynamics) and the transport of hydrogen in the metal (kinetics). The thermodynamics and kinetics are influenced by a number of factors including the fugacity of hydrogen at the surface of material, surface phenomena, stress fields, and trapping of hydrogen by microstructural features.

In the context of this brief communication, we focus on three physical aspects of hydrogen as it pertains to hydrogen in metals: (1) the real gas behavior of hydrogen gas and gas mixtures containing hydrogen; (2) the effect of stress on equilibrium hydrogen content and transport; and (3) effects of hydrogen trapping on hydrogen dissolution and transport. 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 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 this inside 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, is 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, the effects of hydrogen trapping depend on several parameters, resulting in a wide range of possibilities. To illustrate the spectrum of hydrogen trapping on 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 (γ-SS), the effects of hydrogen trapping are relatively small.

These physical phenomena provide a general understanding of hydrogen concentration and distribution of hydrogen in metals. 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 [1-3], Sofronis and colleagues have integrated the thermodynamics and transport equations into comprehensive mechanics-based models and applied these models to engineering structures {Dadfarnia, 2006 #292}.

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:

$$\tfrac{1}{2}\mathrm{H}_2 \leftrightarrow \underline{\mathrm{H}} \tag{1}$$

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

$$\tfrac{1}{2}\left[\mu^o_{HH} + RT\ln\left(f_{HH}/f^o_{HH}\right)\right] = \mu^o_H + RT\ln a_H \tag{2}$$

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:

$$K = \frac{c_o}{f^{1/2}} \tag{3}$$

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:

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

where ΔG^o and ΔH^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 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 [4, 5]. On the other hand, for common engineering conditions, a simple one-parameter equation of state provides an accurate prediction of the real gas behavior of hydrogen (and many other gases) [6]. This Abel-Noble equation of state has the form

$$V_m = \frac{RT}{P} + b \tag{5}$$

where b is the co-volume constant. The constant b can be thought of as the volume of the molecules and the Abel-Noble relationship generally works for conditions where the volume of the ideal gas (RT/P) is larger than b. For hydrogen, it was found that a single value of $b = 15.84$ cm^3/mol describes the real gas behavior for a wide range of conditions appropriate to engineering infrastructure: $T > 223$ K and $P < 200$ MPa [7].

For determining lattice hydrogen concentrations, we require knowledge of the fugacity of the gas (equation 3). The fugacity can be derived from the Abel-Noble equation [7] and can be expressed as a ratio with respect to pressure (sometimes referred to as the fugacity coefficient):

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

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

$$f_i = x_i f \tag{7}$$

The assumption of an ideal mixture should not be confused with ideal gas behavior: it simply means that a gas molecule "sees" all other gas molecules in the system as equivalent, which should be a reasonable assumption for gases in the range of applicability of the Abel-Noble equation of state (since the Abel-Noble equation implies that accounting for interactions between the gas molecules–other than momentum, or "hard-sphere", interactions–is not necessary to describe the state of the gas). 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

$$\frac{f_{HH}}{p_{HH}} = \exp\left(\frac{P}{RT}b\right) \tag{8}$$

This relationship shows that the fugacity of hydrogen in a gas mixture will be greater than pure hydrogen at p_{HH} but less than pure hydrogen at the total pressure P.

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 their effects on hydrogen-assisted fracture.

The concentration of hydrogen dissolved in a metal lattice under stress (c_L, moles of hydrogen per mole of metal atoms) can be determined from the fundamental principles of thermodynamics. Generally, this is expressed as [8, 9]

$$\frac{c_L}{c_o} = \exp\left(\frac{\sigma V_H}{RT}\right) \tag{9}$$

where σ 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 steel is about 2 cm^3/mol [9, 10]). 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 have been modeled by Sofronis using fundamental thermodynamic relationships and the phenomenological laws for diffusion to evaluate the effects of stress on the diffusivity of hydrogen in metals [11]. He found that the effective diffusivity in a metal under stress (D_s) can be related to the diffusivity in a stress-free lattice (D) by

$$\frac{D_S}{D} = 1 + \frac{c_o}{V_M}\left[\frac{2}{9}\frac{E}{(1-\nu)}\frac{{V_H}^2}{RT}\right] \tag{10}$$

where E and ν are the material's elastic constants, 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 [12]:

$$\frac{\theta_T}{1-\theta_T} = \frac{\theta_L}{1-\theta_L}\exp\left(\frac{W_B}{RT}\right) \tag{11}$$

where θ_L is the fraction of available lattice sites that are occupied by hydrogen and θ_T is the fraction of filled trapping sites. In structural metals, the fraction of lattice sites occupied by hydrogen is small, thus $\theta_L << 1$. The concentration of trapped hydrogen (c_T) can be determined in terms of the lattice hydrogen (c_L), concentration of hydrogen traps (n_T) and concentration of lattice sites (n_L):

$$\frac{c_T}{c_L} = \frac{n_T}{\left[c_L + n_L \exp\left(\frac{-W_B}{RT}\right)\right]} \tag{12}$$

where the concentrations and sites are related by $c_L = \beta n_L \theta_L$, and $c_T = \alpha n_T \theta_T$.

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 (equation 12) [12]:

$$\frac{D_{eff}}{D} = \frac{1}{1 + \partial c_T / \partial c_L} = \frac{1}{1 + \frac{c_T}{c_L}(1 - \theta_T)} \tag{13}$$

Equations 12 and 13 are generally expressed in terms of atoms and atomic sites per unit volume, where for example the number of lattice sites per unit volume N_L is equivalent to $n_L N_A / V_M$ (and N_A is Avogardo's number for the definition of a mole). In the formulation presented above, we use moles of hydrogen per mole of metal (also expressed as H/M) and moles of sites 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

The ratio of the fugacity to the partial pressure of hydrogen is a function of the total pressure, and equivalent to the exponential term in equation 6. The ratio *f/P* is typically less than 2 (the dotted lines in Figure 1) for ambient temperature, but less than 1.14 for pressure < 15 MPa (~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 methane and hydrogen at room temperature, assuming that the methane is inert with respect to hydrogen and considering the real gas behavior of the gas mixture. As is shown in Figure 1 for a gas mixture with

P = 100 MPa, f_{HH}/p_{HH} is largest when the p_{HH} is lowest and converges to the value for pure hydrogen state as p_{HH} approaches P. Similar curves can be developed for other values of P. In general, an increase in fugacity due to the presence of the other gases is modest unless the total pressure P is very large compared to partial pressure of hydrogen p_{HH}. For a hydrogen-methane mixture at pressure of 15 MPa with hydrogen partial pressure of 5 MPa, f_{HH}/p_{HH} = 1.13. The value of c_o for this gas mixture is increased by 6% compared to the value predicted for the ideal hydrogen gas at 5 MPa (ignoring the role of stress).

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 H_2 and D_2 [13]. In this case, due to reduced partial pressure, the concentration of dissolved isotopes is less than might be expected based on a system of H_2 and 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 local equilibrium 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 tension, high-strength materials will tend to have higher hydrogen contents due to the greater stresses in the material. Sofronis and collaborators have modeled hydrogen transport and the enhanced hydrogen content at defects in steels [1, 3] and superalloys [2].

In the case of compressive stresses, the hydrogen content is lowered as shown in 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. The combination of compressive stress and lower hydrogen content can, in principle, reduce crack initiation and crack propagation compared to in the absence of these compressive residual stresses.

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 trap sites (n_T), as well as the available lattice hydrogen. 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 [14]: $c_L = 10^{-7}$ H/M (moles of H atoms per mole of metal). The higher energy trap is characteristic of iron [10, 14] 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 [15] resulting in $\theta_T << 1$. Low-energy hydrogen traps, thus, have little impact on hydrogen content except at the 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 [16]. 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 number of available trapping sites is high (generally 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 independent of stress and dependent linearly on c_o (equation 10) [11]. The magnitude of this change, however, is relatively modest. The diffusivity of hydrogen in a stress field D_s relative to the lattice diffusivity of hydrogen is plotted in Figure 5 and shows that for low c_o ($<<10^{-4}$ H/M for iron) the diffusivity is unaffected by stress. For alloys with high solubility such as stainless steels [7], however, the increase of diffusivity in high-pressure hydrogen gas could be around 5% at room temperature ($c_o \sim 0.001$ H/M), and perhaps as high as 20% at elevated temperature ($c_o \sim 0.01$ H/M). 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 [9, 17, 18], consistent with the analysis above. Plastic strains, on the other hand, generate additional sites for hydrogen trapping, thus deformation affects hydrogen trapping and hydrogen transport [2, 3, 14]. As shown by equation 14, 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 ($\theta_T \sim 0$), D_{eff}/D will equal the fraction of hydrogen in lattice sites: $D_{eff}/D = c_L/(c_T + c_L)$. 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 may only be encountered in the initially upon hydrogen exposure. If the trap energy is high, the trap sites will be effectively saturated at equilibrium and $D_{eff}/D \approx 1$. In practice, when trapping is active, D_{eff} is a function of composition (equation 13) and the apparent (or measured) diffusivity represents a time-averaged value that depends on the specifics of the experiment (hydrogen fugacity, geometry, etc.). This explains the inconsistency of hydrogen diffusivity reported at near ambient temperature, compared to the consistent values measured at elevated temperature. At elevated temperature, the concentration dependence of the diffusivity is eliminated because hydrogen trapping is essentially deactivated as shown by the condition $\theta_T \approx 0$ (Figure 6). The measured diffusivity is then 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 [1-3].

SUMMARY

In summary, the thermodynamics and kinetics of hydrogen dissolution and transport in metals is 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, although equilibrium concentrations of hydrogen are proportional to the square of the fugacity. The effects of residual and applied stresses on dissolved hydrogen contents are of similar 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 at ambient temperature significantly increases hydrogen content in the steel and substantially reduces the effective hydrogen diffusivity during transient transport. At elevated temperature (>600 K), the hydrogen traps are inactive. Hydrogen trapping in austenitic stainless steels is predicted to have little affect 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.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

REFERENCES

1. J. Lufrano and P. Sofronis, *Acta Mater* **46,** 1519 (1998).
2. J. Lufrano, P. Sofronis and D. Symons, *Eng Fract Mech* **59,** 827 (1998).
3. M. Dadfarnia, P. Sofronis, I. M. Robertson, B. P. Somerday, G. Muralidharan and D. Stalheim, Proceedings of ASME International Mechanical Engineering Congress and Exposition (IMECE2006), 2006, Chicago IL. ASME (2006).
4. H. Hemmes, A. Driessen and R. Griessen, *J Phys C Solid State* **19,** 3571 (1986).
5. M. Tkacz and A. Litwiniuk, *J Alloy Compd* **330-332,** 89 (2002).
6. D. R. Chenoweth, SAND83-8229 Sandia National Laboratories, Livermore CA (1983).
7. C. San Marchi, B. P. Somerday and S. L. Robinson, *Int J Hydrogen Energy* **32,** 100 (2007).
8. J. O. M. Bockris and P. K. Subramanyan, *Acta Metall* **19,** 1205 (1971).
9. J. O. M. Bockris, W. Beck, M. A. Genshaw, P. K. Subramanyan and F. S. Williams, *Acta Metall* **19,** 1209 (1971).
10. J. P. Hirth, *Metall Trans* **11A,** 861 (1980).
11. P. Sofronis, *J Mech Phys Solids* **43,** 1385 (1995).
12. R. A. Oriani, *Acta Metall* **18,** 147 (1970).
13. C. San Marchi, B. P. Somerday, R. S. Larson and S. F. Rice, *J Nucl Mater* **372,** 421 (2008).
14. A. J. Kumnick and H. H. Johnson, *Acta Metall* **28,** 33 (1980).
15. G. J. Thomas, *Hydrogen Effects in Metals*. Proceedings of the Third International Conference on Effect of Hydrogen on Behavior of Materials (Moran WY, 1980), volume IM Bernstein and AW Thompson, editors. New York: The Metallurgical Society of AIME (1981) p. 77.

16. H. G. Nelson and J. E. Stein, NASA TN D-7265. Ames Research Center, National Aeronautics and Space Administration, Moffett Field CA (April 1973).
17. A. M. Brass, J. Chene, G. Anteri, J. Ovejero-Garcia and L. Castex, *J Mater Sci* **26,** 4517 (1991).
18. B. E. Wilde and I. Chattoraj, *Scr Metall Mater* **26,** 627 (1992).

Table 1. Material properties and parameters used in calculations.

Property	Units†	Value	Reference
Hydrogen Gas			
b	cm^3/mol	15.84	[7]
Metal			
V_M	cm^3/mol	7.1	—
E	GPa	200	—
v	—	0.33	—
Hydrogen in metal			
V_H	cm^3/mol	2	[9, 10]
Hydrogen in iron			
W_B	kJ/mol	60	
K_o	H/M $MPa^{-1/2}$	0.00171	[14]
ΔH^o	kJ/mol	27.2	
Hydrogen in austenitic stainless steel			
W_B	kJ/mol	20	[15]
K_o	H/M $MPa^{-1/2}$	0.00192	[7]
ΔH^o	kJ/mol	5.9	

† H/M = moles of H atoms per mole of metal atoms

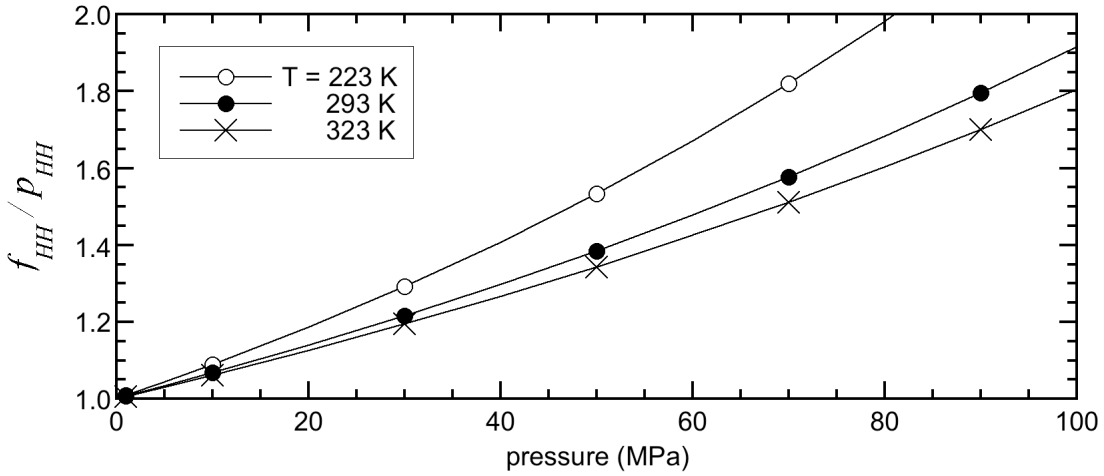

Figure 1. Ratio of hydrogen fugacity to hydrogen partial pressure as a function of total system pressure.

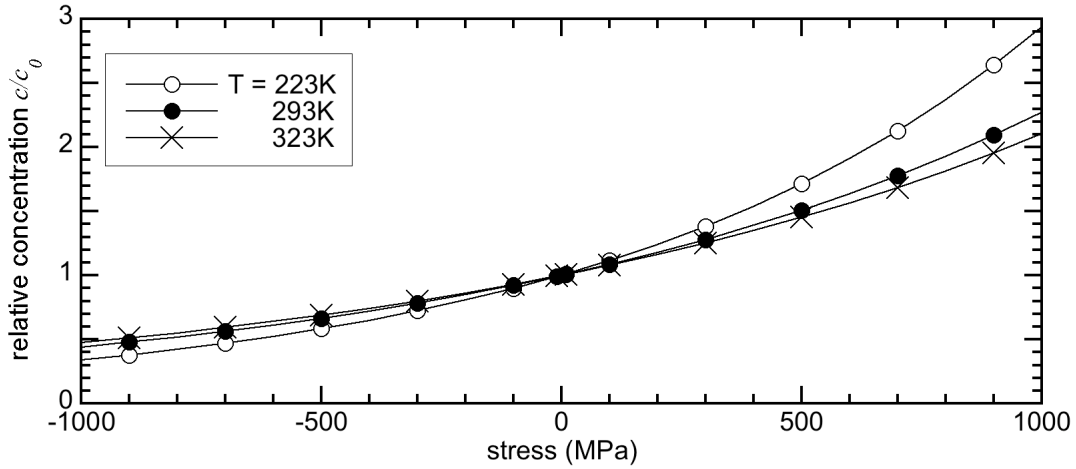

Figure 2. Relative concentration of hydrogen as a function of equivalent hydrogen static stress.

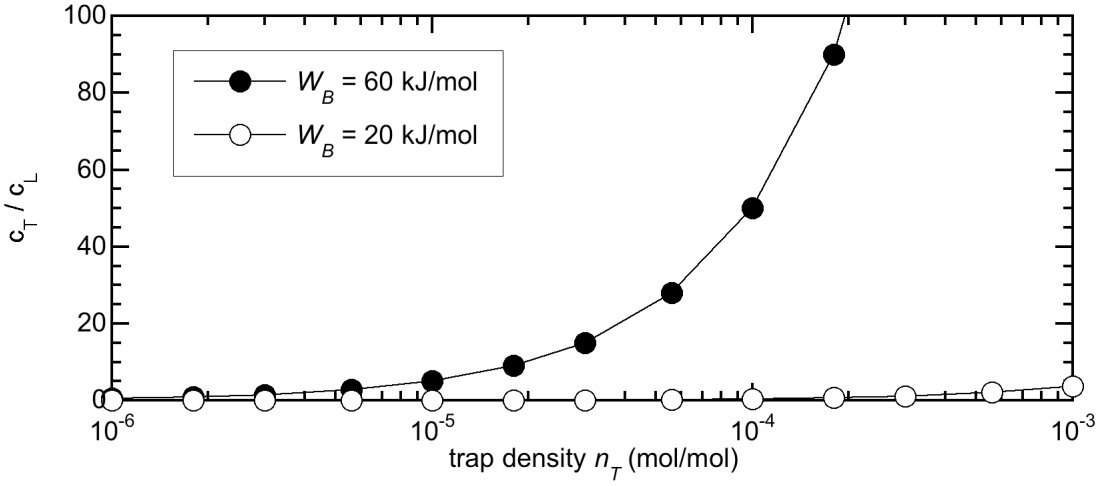

Figure 3. The concentration of trapped hydrogen (c_T) relative to lattice hydrogen (c_L) as a function of the density of trap sites (n_T).

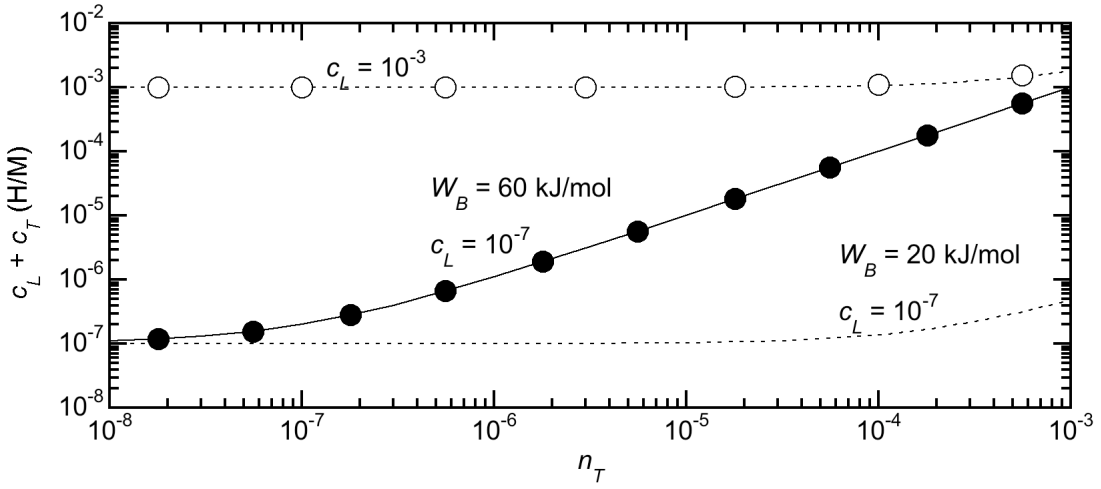

Figure 4. The total concentration of hydrogen as a function of the density of trap sites (n_T). The curves for the two binding energies (W_B) with $c_L = 10^{-3}$ are essentially indistinguishable.

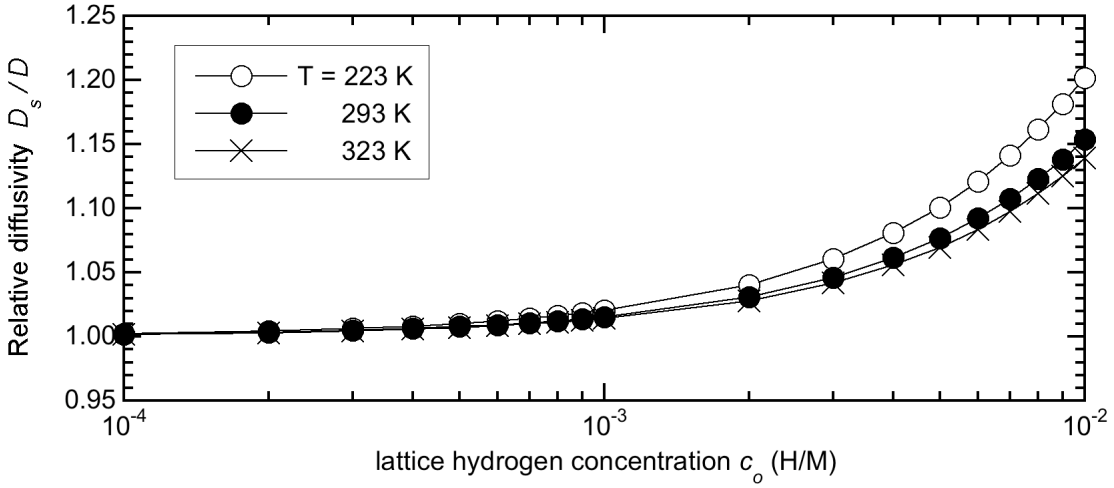

Figure 5. The effective diffusivity due to stress relative to the lattice (stress-free) diffusivity (D_s/D) as a function of lattice hydrogen concentration.

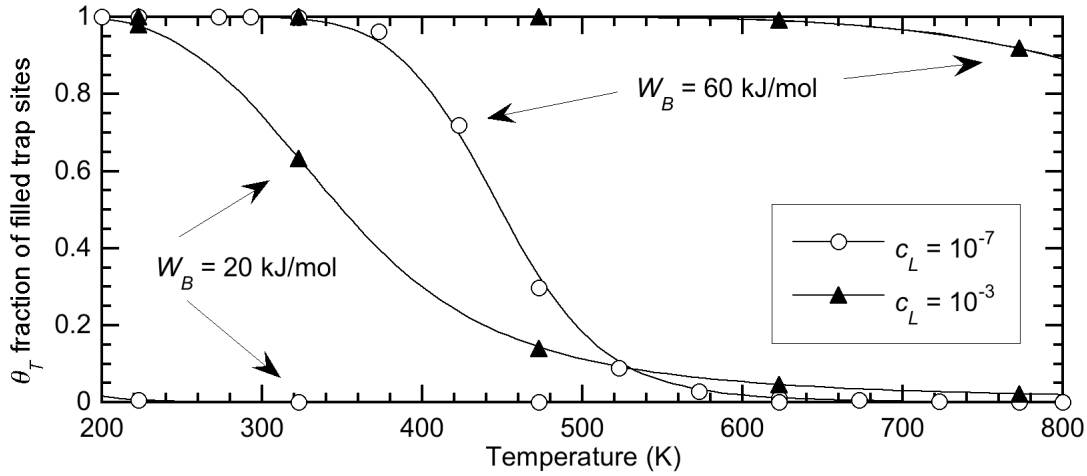

Figure 6. The fraction of filled traps as a function of temperature.