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Letter to the Editor

Solubility of hydrogen and its isotopes in metals from mixed gases

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Abstract

This short communication reviews the classical thermodynamics governing dissolution of hydrogen in metals. Classical thermodynamics is then applied to equilibrium dissolution of hydrogen and its isotopes in metals from mixtures of their diatomic gases. For simplicity in presentation, we use the specific example of H_2 and D_2 gas mixtures to demonstrate the general principles of equilibrium solubility; however, other systems may be treated analogously. The formation of HD gas is shown to have a significant effect on equilibrium solubility since it affects the chemical potentials of the H_2 and D_2 gases. Finally, we compare this thermodynamic analysis with empirical solutions from the literature.

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1. Introduction

The solubility of atomic hydrogen in metals at equilibrium with hydrogen gas is well-documented in the literature for a number of important engineering metals [1,2]. The solubility of hydrogen and its isotopes in metals from mixtures of these gases has also been studied in the literature, applying empirical relationships to model equilibrium dissolution of hydrogen isotopes. In particular, Hickman assumes that mixtures of hydrogen and deuterium gases behave as a one-component gas with an effective solubility constant that follows a linear mixing rule [3]; this assumption has been propagated in the literature [4–9] without consideration of the fundamental thermodynamics of dissolution. In the following presentation, we use classical thermodynamics to describe equilibrium dissolution of hydrogen and deuterium in metals from the gas phase and compare these results to empirical relationships from the literature.

2. Thermodynamics of dissolution

2.1. One-component gas system

The fundamental thermodynamic description of hydrogen gas in equilibrium with atomic hydrogen in a metal ($\frac{1}{2}H_2 \leftrightarrow \underline{H}$) can be expressed as

$$\mu_{\mathrm{H}}^{\theta} + RT\ln x_{\mathrm{H}} = \frac{1}{2}\left(\mu_{\mathrm{HH}}^{\mathrm{o}} + RT\ln\frac{p_{\mathrm{HH}}}{p^{\mathrm{o}}}\right), \tag{1}$$

where $\mu_{\mathrm{H}}^{\theta}$ is the Henrian standard state for atomic hydrogen (i.e., at infinite dilution the activity of hydrogen equals the mole fraction of hydrogen: $a_{\mathrm{H}} = x_{\mathrm{H}}$), $\mu_{\mathrm{HH}}^{\mathrm{o}}$ is the chemical potential of hydrogen gas at a standard pressure of p^{o}, p_{HH} is the partial pressure of hydrogen gas (fugacity should be used rigorously, but for ease of presentation we assume an ideal gas), R is the universal gas constant and T is the temperature in Kelvin. Throughout this text, we use a single subscript letter to represent the atomic state dissolved in a metal lattice, and we use a pair of letters to represent the diatomic gas. The thermodynamic equilibrium expressed by Eq. (1) can also be written in the form

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$$\exp\left(\frac{-\Delta G_{\mathrm{f}}^{0}(\underline{H})}{RT}\right)=\frac{x_{\mathrm{H}}}{(p_{\mathrm{HH}}/p^{\mathrm{o}})^{1/2}}, \tag{2}$$

where $\Delta G_{\mathrm{f}}^{0}(\underline{H})$ is the free energy of formation of atomic hydrogen in the metal lattice from the gas at standard state. Alternatively, Eq. (2) can be written in the familiar form of Sievert's Law using nonspecific concentration units c_{H} and employing the equilibrium constant K_{H}, which represents the thermodynamic driving force for the dissolution reaction and is often called the solubility (or Sievert's constant):

$$K_{\mathrm{H}}=\frac{c_{\mathrm{H}}}{p_{\mathrm{HH}}^{1/2}}. \tag{3}$$

The exponential form of the K_{H} and its relationship to basic thermodynamic properties is evident from Eqs. (2) and (3).

2.2. Two-component gas system

Now, we consider an ideal mixture of H_2 and D_2 gases in equilibrium with atomic hydrogen and deuterium in a metal. In the limit of dilute solid solutions (which is generally the case for dissolution of hydrogen isotopes in engineering metals), the equilibria for both hydrogen and deuterium are described by independent relationships with the same form as Eqs. (1) and (2). In other words, the concentrations of dissolved hydrogen and deuterium are, respectively, proportional to the square-root of the partial pressure of each gas, determined independently from Eq. (3):

$$c_{\mathrm{H}}=K_{\mathrm{H}}(p_{\mathrm{HH}}^{*})^{1/2}=(x_{\mathrm{HH}}^{*})^{1/2}K_{\mathrm{H}}P^{1/2}, \tag{4}$$

$$c_{\mathrm{D}}=K_{\mathrm{D}}(p_{\mathrm{DD}}^{*})^{1/2}=(x_{\mathrm{DD}}^{*})^{1/2}K_{\mathrm{D}}P^{1/2}, \tag{5}$$

where $p_i = x_iP$, x_i is the mole fraction of i in the gas phase, P is the system pressure, and the asterisk denotes the partial pressure or mole fraction of each component in the two-component system. The partial pressures of H_2 and D_2 are assumed to remain constant in the two-component gas (valid if the volume of metal is small compared to the volume of gas, so that the partial pressures of the gases are unaffected by dissolution into the metal lattice).

The difference between K_{H} and K_{D} will depend on values of $\Delta G_{\mathrm{f}}^{0}$ for the respective atoms in the metal of interest, although generally $\Delta G_{\mathrm{f}}^{0}$ is not known as a function of isotope. Since the free energies of the monatomic gases (Table 1) differ by only a few percent, we expect that for dilute solid solutions $\Delta G_{\mathrm{f}}^{0}(\underline{H}) \approx \Delta G_{\mathrm{f}}^{0}(\underline{D})$ for metals that do not strongly interact with hydrogen (for example metals that do not form hydrides, such as stainless steels). Consequently, K will be approximately independent of isotope in metals [10] that do not have a strong affinity for hydrogen and that do not have microstructural sites that strongly trap hydrogen or its isotopes. On the other hand, a relatively small isotope effect on solubility has been reported in strong hydride formers such as palladium [3–6], as well as in stainless steel [1]. In order to keep our analysis general, we will therefore assume that $K_{\mathrm{H}} \neq K_{\mathrm{D}}$. For a more comprehensive evaluation of isotope effects, see Ref. [11].

Table 1
Thermodynamic properties of hydrogen and deuterium gases at standard state (pressure = 1 bar) and temperature of 298.15 K

	$\Delta G_{\mathrm{f}}^{\mathrm{o}}$ (kJ mol^{-1})	$\Delta H_{\mathrm{f}}^{\mathrm{o}}$ (kJ mol^{-1})	(J mol^{-1} K^{-1})	Ref.
H_2 (g)	0	0	130.68	[16,17]
D_2 (g)	0	0	144.96	[16,17]
HD (g)	−1.463	0.32	143.80	[16,17]
H (g)	203.28	218.00	114.72	[16,17]
D (g)	206.55	221.72	123.35	[17]

The total concentration of atomic hydrogen and deuterium dissolved in the metal is the sum of Eqs. (4) and (5):

$$c_{\mathrm{H}}+c_{\mathrm{D}}=\left[(x_{\mathrm{HH}}^{*})^{1/2}K_{\mathrm{H}}+(x_{\mathrm{DD}}^{*})^{1/2}K_{\mathrm{D}}\right]P^{1/2}. \tag{6}$$

Although this is theoretically correct given the assumptions, permeability and solubility studies of H_2–D_2 gas mixtures show that this relationship predicts values greater than measured experimentally [3–5,9]. To explain experimental data, Hickman empirically proposed a linear rule of mixtures for the solubility [3], such that the total isotope concentration has the form

$$c_{\mathrm{H}}+c_{\mathrm{D}}=[x_{\mathrm{HH}}^{*}K_{\mathrm{H}}+x_{\mathrm{DD}}^{*}K_{\mathrm{D}}]P^{1/2}. \tag{7}$$

In that report, it was acknowledged that if the dissolution of hydrogen and deuterium were thermodynamically independent, each atomic concentration in the metal would theoretically be proportional to the square-root of the partial pressure of the respective gas as expressed in Eqs. (4) and (5), e.g., $c_{\mathrm{H}} \propto (x_{\mathrm{HH}}^{*})^{1/2}$. Hickman equated the empirical result with $c_{\mathrm{H}} \propto x_{\mathrm{HH}}^{*}$ (Eq. (7)) to treating the hydrogen and deuterium as a one-component gas. From a thermodynamic perspective, however, hydrogen and deuterium are distinct and therefore mixtures of these gases should not be treated as a one-component gas.

A clear theoretical basis for using relationships nominally equivalent to Eq. (7) in lieu of the square-root dependence of Eq. (6) has not been clearly established in the literature, even though experimental data matches the lower concentrations predicted by the empirical relationship. The explanation for smaller concentrations in experimental studies compared with the theoretical predictions of Eq. (6) is simple: isotopic exchange between H_2 and D_2 produces HD gas and thereby reduces the partial pressures of both H_2 and D_2 gases [10,12]. Hickman and others have not recognized the significance of the HD equilibrium [3–9], in some cases purposely neglecting it. Some studies on permeation of multi-component gases, on the other hand, have included the gas-phase equilibrium in their analyses [10,12]. In the next section, we formulate the HD equilibrium, which we call the three-component system, in the context of this problem. Subsequently, we discuss the results of this thermodynamic analysis and show that the analysis of the three-component system reduces to the empirical relationship (Eq. (7)) for specific conditions.

2.3. Three-component gas system

Consider a system that initially contains only H_2 and D_2 gases with partial pressures of p^*_{HH} and p^*_{DD}. Allow the system to come to equilibrium with respect to the formation of HD gas, such that three gases coexist at equilibrium: H_2, D_2 and HD. Also allow thermodynamic equilibrium to be established between the mixed gas and each isotope in the metal (Eq. (3)). For a given temperature and system pressure, there are five unknowns that describe the gas-phase equilibrium and the equilibria of dissolution of the isotopes: the partial pressures of the three gases (p_{HH}, p_{DD} and p_{HD}) and the concentrations of hydrogen and deuterium in the metal (c_H and c_D). Atom conservation provides two of the five equations necessary to describe the system completely at equilibrium:

$$x^*_{HH} = x_{HH} + \tfrac{1}{2}x_{HD}, \qquad (8)$$

$$x^*_{DD} = x_{DD} + \tfrac{1}{2}x_{HD}, \qquad (9)$$

where the 'two-component' mole fractions of hydrogen (x^*_{HH}) and deuterium (x^*_{DD}) represent the relative number of hydrogen and deuterium atoms in the system, and x_{HH}, x_{DD}, and x_{HD} represent the equilibrium mole fractions of the gas species H_2, D_2 and HD, respectively. Clearly, $x_{HH} < x^*_{HH}$, and therefore, $p_{HH} < p^*_{HH}$; similarly for deuterium. The three additional equations come from thermodynamic equilibria for the following reactions:

$$H_2 + D_2 \leftrightarrow 2HD \qquad (10)$$

$$\tfrac{1}{2}H_2 \leftrightarrow \underline{H} \qquad (11)$$

$$\tfrac{1}{2}D_2 \leftrightarrow \underline{D} \qquad (12)$$

These equilibria represent an equivalence of chemical potential; for example, the chemical potential associated with hydrogen in the gas phase must be equivalent to the chemical potential associated with hydrogen in the metal, which is the essential meaning of Eq. (3) and is implicit in Eq. (11). Additional equilibria can be identified, such as the equilibrium between the HD gas molecule and atoms of H and D dissolved in the metal; however, this equivalence of chemical potential is already implied in Eqs. (10)–(12) (indeed, it can be expressed as a linear combination of these equations).

The equilibrium composition of the gas phase can be determined based on Eq. (10) using the principles of classical thermodynamics, giving

$$K_{HD} = \frac{p^2_{HD}}{p_{HH}p_{DD}} = \frac{x^2_{HD}}{x_{HH}x_{DD}}. \qquad (13)$$

The equilibrium constant K_{HD} is determined from the thermodynamic properties of HD (Table 1) analogously to Eq. (2) (see also Refs. [13,14]):

$$K_{HD} = \exp(-2\Delta G^o_f(HD)/RT) = 4.21\exp(-76.97/T). \qquad (14)$$

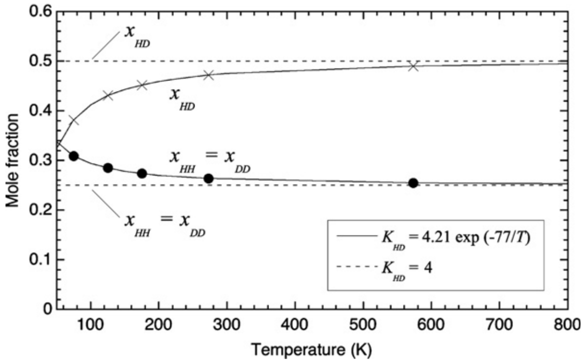

Fig. 1. Mole fraction of gases as a function of temperature for system with equal moles of hydrogen and deuterium: $x^*_{HH} = x^*_{DD} = 0.5$.

At ambient temperature (25 °C), K_{HD} has a value of 3.25. With knowledge of x^*_{HH}, x^*_{DD} and the temperature, Eq. (13) can be solved for the equilibrium mole fractions of the three gases by substitution of Eqs. (8) and (9) (which involves solving a relatively simple quadratic equation). Statistical thermodynamic arguments lead to the assumption that $K_{HD} \sim 4$ [12,15], which while approximately correct at ambient and elevated temperatures, is not accurate at low temperature. This is demonstrated in Fig. 1, where the equilibrium mole fractions of the gases are plotted as a function of temperature for an equiatomic H–D gas mixture, highlighting the difference between the temperature-dependent solution and the statistical limit (i.e., between $K_{HD} = 4.21\exp(-76.97/T)$ and $K_{HD} = 4$).

The forms of the equilibria representing the isotopes in the metal (from Eqs. (11) and (12)) are essentially unchanged by the formation of the HD phase and are analogous to Eqs. (4) and (5) with the equilibrium partial pressures or mole fractions in place of the hypothetical two-component values:

$$c_H = K_H p^{1/2}_{HH} = (x_{HH})^{1/2} K_H P^{1/2}, \qquad (15)$$

$$c_D = K_D p^{1/2}_{DD} = (x_{DD})^{1/2} K_D P^{1/2}. \qquad (16)$$

In other words, the equilibrium embodied in Eq. (3) remains applicable for each of the isotopes individually, and the formation of HD simply reduces the partial pressures of H_2 and D_2. Therefore, the expression for the total equilibrium concentration of atomic hydrogen and deuterium dissolved in the metal is similar to Eq. (6) except that the equilibrium mole fractions of the gases (x_{HH} and x_{DD}) must be used in place of the two-component mole fractions (x^*_{HH} and x^*_{DD}):

$$c_H + c_D = [(x_{HH})^{1/2}K_H + (x_{DD})^{1/2}K_D]P^{1/2}. \qquad (17)$$

3. Discussion of models

Analysis of the two-component system, which neglects HD formation (Eq. (6); cf. also [3], as well as case 1 in

Refs. [4,5]), results in a total hydrogen isotope concentration that is generally greater than would be expected for a one-component hydrogen gas at the same total system pressure (provided that K_{H} and K_{D} have similar magnitudes). This is due to the dependence of the atomic concentration on the square-root of the partial pressure. The total isotope concentration in the three-component system (Eq. (17) with the mole fractions determined from K_{HD} as a function of temperature) is also less than predictions from the two-component system as shown in Fig. 2 for equal parts hydrogen and deuterium. Since the formation of HD gas reduces the partial pressures (and the chemical potentials) of H_2 and D_2, the concentration of hydrogen and deuterium in the metal must also be corresponding lower in the three-component system compared to the two-component system. Incidentally, adding HD to a system of H_2 and D_2 (without changing the ratio of H to D atoms) will not change the equilibrium that must be established between these three gases; thus the addition of HD to a system of H_2 and D_2 (while maintaining the same total pressure) will have no effect on the total concentration of the isotopes that dissolve into the metal [12].

The empirical relationship (Eq. (7)) is also plotted in Fig. 2, showing that it is approximately equivalent to the result for the three-component system (i.e., with HD formation); the difference between these two solutions is less than 5% for $T > 200$ K. The similarity between the empirical relationships from the literature and the thermodynamic solution of the three-component system can be shown algebraically using the statistical limit for K_{HD}. Substituting Eqs. (8) and (9) into Eq. (13) with $K_{\mathrm{HD}} = 4$, a simple relationship can be established between the equilibrium mole fractions of the diatomic gases (x_{HH} and x_{DD}) and the two-component mole fractions (x^*_{HH} and x^*_{DD}):

$$x_{\mathrm{HH}} \sim (x^*_{\mathrm{HH}})^2, \tag{18}$$

$$x_{\mathrm{DD}} \sim (x^*_{\mathrm{DD}})^2. \tag{19}$$

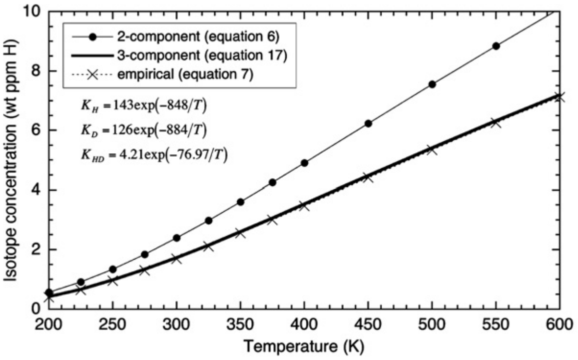

Fig. 2. Total isotope concentration as a function of temperature in type 347 stainless steel with $p^*_{\mathrm{HH}} = p^*_{\mathrm{DD}} = 0.05$ MPa. K_{H} and K_{D} are in units of wt ppm H MPa$^{-1/2}$ from Ref. [1]; K_{HD} has no units. Note units are incorrectly given in Ref. [1], see Appendix of Ref. [2].

At ambient and elevated temperatures where $K_{\mathrm{HD}} \sim 4$ (Fig. 1), Eqs. (18) and (19) can be substituted into Eq. (17) to yield

$$c_{\mathrm{H}} + c_{\mathrm{D}} \sim (x^*_{\mathrm{HH}} K_{\mathrm{H}} + x^*_{\mathrm{DD}} K_{\mathrm{D}}) P^{1/2}. \tag{20}$$

This is the empirical result that one finds in the literature [3–8], i.e., Eq. (7). Experimental studies of both solubility and permeability in palladium support the empirical solution, which provides the same result as a complete equilibrium thermodynamic analysis accounting for the formation of HD gas (Fig. 3).

It is important to note the basic assumptions used to develop these results. We have assumed that hydrogen isotopes dissolve into the metal forming a dilute solution. This assumption is implicit in Sievert's Law and may not be applicable under some conditions; for example, Sievert's Law may be inappropriate for strong hydride formers under conditions when chemical bonding should be considered, or otherwise when the dilute solution approximation is inappropriate. For structural steels at equilibrium the assumptions implicit in Sievert's Law are generally satisfied, as they are in palladium at low pressure. At cryogenic temperatures, when the kinetics of these reactions are very slow, it might be expected that the formation of HD will be effectively suppressed. However, the physical processes, such as surface adsorption and dissociation kinetics, that affect the formation of HD also affect the dissolution of hydrogen and deuterium into the metal, so establishing equilibrium in one phase (solid) but not the other (gas) seems unlikely. Applicability of an equilibrium analysis, such as that provided here, should, in any case, be evaluated with respect to the relevant kinetics and time scales of interest.

In summary, while empirical relationships from the literature for the solubility of hydrogen and its isotopes in metals from mixtures of the diatomic gases provide useful predictions, they do not reflect an obvious accounting for the thermodynamics of the system. The empirical relationships appear to violate basic thermodynamic principles since H_2 and D_2 must establish independent equilibria with

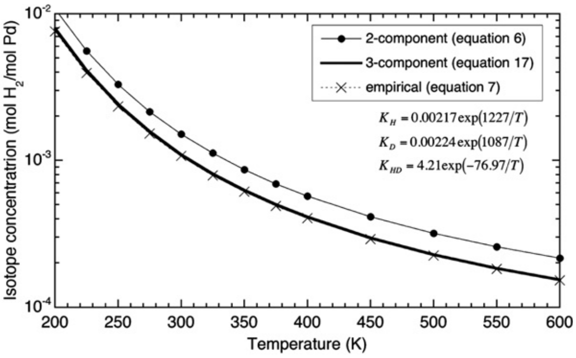

Fig. 3. Total isotope concentration as a function of temperature in palladium with $p^*_{\mathrm{HH}} = p^*_{\mathrm{DD}} = 50$ Pa. K_{H} and K_{D} are in units of (mol H_2/mol Pd) MPa$^{-1/2}$ from Ref. [4]; K_{HD} has no units.

the metal, which due to equivalence of chemical potential (i.e., Sievert's Law) must contain a square-root dependence on pressure (and mole fraction of the isotope in the gas phase). Only when $K_{\mathrm{HD}} \sim 4$ does the thermodynamic solution ($c_{\mathrm{H}} \propto x_{\mathrm{HH}}^{1/2}$) reduce to the empirically-deduced solution ($c_{\mathrm{H}} \propto x_{\mathrm{HH}}^{*}$).

We note in closing that the general solutions to equilibria that involve a gas require use of fugacity in place of pressure. For the development described here we use the pressure in thermodynamic relationships (ideal gas assumption), although for mixtures of hydrogen and its isotopes the use of fugacity does not change the form of the solutions found here for ambient and elevated temperature: fugacity of hydrogen and deuterium can be substituted for the partial pressure of hydrogen and deuterium, respectively, in these relationships. The reader is referred to Ref. [2] for more details about fugacity of hydrogen and its isotopes.

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