Comment on "A Statistical−Mechanical Method To Evaluate Hydrogen Solubility in Metal"

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Introduction

In a recent paper, Ogawa[1] has proposed a statistical-mechanical method based on the so-called site-occupying model (SOM) to evaluate hydrogen solubility in metals. Ogawa claims that SOM is in much better agreement with experimental data than site blocking models (SBM). I am at variance with this opinion. The objective of this paper is to compare both approaches. I shall restrict myself to the configurational contribution to the partial molar mixing entropy of hydrogen, which concentrates on the main points of divergences.

Thermodynamics of Metal Hydrides

Following the classical work of Lacher[2] on the palladium−hydrogen system, the partial molar mixing entropy of hydrogen is generally written with a good approximation:

$$\Delta S(\text{H}) = \bar{S}_{\text{conf}} + \bar{S}_{\text{nonconfig}} - \frac{1}{2}S^0(\text{H}_2) \ (\text{gas}) \qquad (1)$$

In this expression, $\bar{S}_{\text{conf}}$ is the configurational contribution to the partial molar entropy. This term is temperature independent. Let us consider the simple case of a random distribution of hydrogen atoms toms:

$$\bar{S}_{\text{conf}} = R \ln \frac{n_{\text{s}} - x}{x} \qquad (2)$$

In this expression, x is the ratio of the number of H atoms over the number of metal atoms and n_{s} the number of interstitial sites per metal atom.

$\bar{S}_{\text{nonconfig}} - {}^1/_2 S^0(\text{H}_2)$ is expected to be only weakly temperature dependent. The origin of the term $\bar{S}_{\text{nonconfig}}$ is essentially vibrational. This term can be evaluated using the Einstein model for solute atoms, with a vibrational frequency obtained from peaks of inelastic neutron frequency. This approach is only a first approximation. In fact, as detailed in a number of reviews,[3−6] things are a little bit more complicated. For instance,

• electronic contributions have to be taken into account,[7]

• the vibrational contribution is caused not only by the vibration of H atoms but also by the modification of the vibration of metal atoms,[8−10] and

• interstitial atoms are not randomly distributed (this point will be discussed in the next two sections).

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Site-Occupying Model

It has long been recognized that the expression of the ideal configurational entropy, eq 2, is not satisfying:

(1) The composition dependence of the entropy obtained in this way is too weak.

(2) The experimental limiting value of x is generally smaller than the number of interstitial sites expected from crystallographic arguments, which would be 1 for octahedral sites in cfc lattices such as palladium and 6 for tetrahedral sites in bcc lattices such as V, Nb, and Ta.

(3) It is an experimental fact that two hydrogen atoms in a metal cannot come closer than 0.21 nm.[11]

We have gathered in this section three different models that have a common objective: to decrease the number of available sites.

• For the palladium−hydrogen system, instead of eq 2, Lacher[2] has used

$$\bar{S}_{\text{conf}} = R \ln \frac{0.59 - x}{x} \qquad (3)$$

This choice was based on the rigid band model[12,13] and also on the pressure−composition isotherms of Gillespie and Hall.[14]

• Several years ago for tetrahedral sites in bcc metals, O'Keeffe and Steward[15] considered that relaxation around a dissolved interstitial atom resulted in there being just one interstitial site per metal atom, rather than the six tetrahedral sites per metal atom in the undistorted bcc array. In this way, these authors have used

$$\bar{S}_{\text{conf}} = R \ln \frac{3(1 - x)}{x} \qquad (4)$$

• Very recently for the same systems, from geometrical considerations and also from the experimental work of Veleckis and Edwards,[16] Ogawa[1] has used

$$\bar{S}_{\text{conf}} = R \ln \frac{0.8 - x}{x} \qquad (5)$$

In fact, these treatments are not correct: For Pd−H systems, it has been shown that Lacher was wrong in thinking that the upper limit of H/M is 0.59.[17] In the same way, for hydrogen solutions in bcc systems, it is possible to go beyond the value $H/M = 0.8$ predicted by Ogawa[1] and also beyond the value $H/M = 1$ predicted by O'Keeffe and Steward,[15] as shown by Maeland et al.[18]

Site-Blocking Model

Empirical Models. It has been recognized for several decades that random distribution of interstitial atoms is not always an acceptable approximation. In the case of repulsive interactions, an improvement is to consider that the only restriction to a random distribution is that two neighbor sites cannot be simultaneously occupied. In empirical models,[19−22] the expression of $g(x)$ should be consistent with two constraints: At low concentrations the expression of $\bar{S}_{\text{conf}}$ should be identical to the expression obtained for a random distribution while the expres-

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TABLE 1: Percentage of Deviation for $g(x)$

x	% ideal	% Speiser and Spretnak
0.01	+1.00	−0.003
0.05	+5.24	−0.07
0.10	+11.0	−2.9

sion for large concentrations should be consistent with the solubility limit. A shortcoming of empirical approaches is that in intermediate concentrations, the strength of the blocking effect is underestimated.

Analytical Treatments. More recently, Boureau and Campserveux[23] have proposed a new approach of the blocking model based on a theorem demonstrated by Thorn and Winslow:[24] Let us define $g(x)$ as the number of available sites per metallic atom (an available site is a site which is neither filled nor blocked). Thorn and Winslow have demonstrated that the expression of the configurational contribution to the partial molar entropy is

$$\bar{S}_{conf} = R \ln \frac{g(x)}{x} \tag{6}$$

The calculation of $g(x)$ made by Boureau and Campserveux is essentially a conditional probability calculation. This method has been extended by McKinnon and Dahn[25] to the case of different kinds of lattices.

For bcc metals with six interstitial sites per atom that are tetrahedrally coordinated with respect of the host atom, if first and second nearest neighbor sites are blocked, Boureau has shown[26] that

$$g(x) = \frac{(6 - 4x)^2}{6 - x} \tag{7}$$

is a good approximation.

Now let us discuss the case of dilute solutions. Ogawa claims that in the SBM model, hydrogen atoms can come closer than 0.21 nm. Let us show that this statement is erroneous.

At low concentrations expression eq 7 becomes simplified

$$g(x) = 6 - 7x \tag{8}$$

which is identical to the expression that we would obtain by neglecting the overlap between exclusion spheres, as done by Speiser and Spretnak.[19] Now let us consider the case of very dilute solutions ($x \ll 1$). In the ideal approximation, therefore without blocking,

$$g(x) = 6 - x \tag{9}$$

In Table 1, we have calculated the percentage of error in two crude approximations, assuming that eq 7 is correct.

• Ideal solutions: We use eq 9. $g(x)$ is overestimated because the only restriction to the insertion of a hydrogen atom is that already occupied sites are forbidden.

• An approximation due to Speiser and Spretnak[19] who do not take overlap in consideration, which increases the number of forbidden sites and leads to eq 8.

If $x \ll 0.01$, both approximations are acceptable: The blocking has almost no effect on the number of available sites. A last comment: We have a very similar situation for gas at room temperature. I borrow an example from the classical book of

Atkins:[27] The number of states thermally accessible to an H_2 molecule confined to a 100 cm^3 vessel is about 10^{26}. In other words, at low pressures, most of the quantum states are empty. In this case Bose−Einstein and Fermi−Dirac statistics provide the same (very very small) value for populations of different states, which allows the use of the Maxwell−Boltzmann statistics.

To test the validity of this approach, we have to check two things.

(1) The self-consistency of the model. In other words, if we accept the assumptions underlying this model, we have to be sure that the numerical treatment does not generate appreciable errors. To check this point, we have compared the results provided by our method with exact results for three families of lattices.[23]

• For one-dimensional problems the probability calculations are rigorous.

• The case of a square lattice has been treated in a number of studies[28−33] and has been shown to be in reasonable agreement with our calculations.

• For three-dimensional problems our method provides also calculations in agreement with Monte Carlo calculations.[34]

(2) The relevance of the assumptions of the model for some real systems. This has been confirmed for

• Chevrel compounds,[25]

• solutions of hydrogen in bcc metals,[35] and

• solutions of oxygen in UO_{2+x}.[23]

Conclusion

In this paper, it has been shown that the site blocking model is a reasonable model to understand the solubility of solid solutions with strong repulsions between interstitial atoms. As noted by Boureau,[36] this model is not sophisticated enough to explain the phase diagram. This model has to be improved along the lines proposed by Meuffels and Oates[37] and by MacGillivray et al.[38]

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