Reply to Comment on “A Statistical–Mechanical Method To Evaluate Hydrogen Solubility in Metal”

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My responses to the comments submitted by Boureau⁴ are as follows.

Maeland’s report is a study on the formation of hydride at high hydrogen pressure. However, my paper is limited to the solid solution of hydrogen at a hydrogen pressure of 1 MPa or less and does not consider hydride (see the Introduction (p 2134) and results and Discussion (p 2139) of my paper⁵).

In my paper, the value of \( n_s/\zeta \) is 0.8 for bcc at 1 MPa or less, and so I expect the value of \( n_s/\zeta \) at a pressure exceeding 1 MPa to become larger than that at 1 MPa or less (see section 3.4 (p 2142) in my paper⁵).

My paper uses the Maxwell–Boltzmann statistics (see eq 3 on page 2136 of my paper 1).

At the site-blocking model (SBM), the blocking effect is stronger at higher hydrogen concentration and is negligible at lower hydrogen concentration (the ideal case). This concept is shown in Figure 1.

Ideal case:

\[
S_c = -k \ln \left( \frac{n_H}{n_s - n_H} \right) \quad n_s = 6 \text{ for bcc} \quad (a)
\]

SBM:

\[
S_c = -k \ln \left( \frac{(6 - n_H)n_H}{(6 - 4n_H)^2} \right) \quad (b)
\]

SOM:

\[
S_c = -k \ln \left( \frac{n_H}{\frac{n_s}{\zeta} - n_H} \right) \quad n_s/\zeta = 0.8 \text{ for bcc} \quad (c)
\]

where \( n_s \) is the total number of interstitial sites available for hydrogen atoms per metal atom and \( n_H \) is the atomic ratio of solute hydrogen atoms to metal atoms.

Clearly, this figure shows that the curve of SBM deviates from the curve of the ideal case at higher concentration, and the curve of SBM agrees with the curve of the ideal case at lower concentration. This deviation arises from the blocking effect (this result is essentially the same as Boureau listed the percentage deviation in his Table 1⁵).

A schematic representation of SBM at low concentration (2 atoms) is shown in Figure 2 as an example. This situation means “no blocking effect (i.e., the ideal case)” as Boureau writes.⁴

![Figure 1. Comparison among partial configurational entropies.](image1)

![Figure 2. SBM at low concentration (the ideal case).](image2)

Case 0 means that hydrogen atom A is put in site 1. Next, hydrogen atom B will be put in site 2, 3, 4, 5, or 6. Atom B can be located in 5 ways: cases 1–5. Mathematically, cases 1–5 are allowed (no blocking effect; i.e., this means the ideal case). The number of ways of assigning \( N_H \) distinguishable H atoms from \( N_s \) distinguishable sites is given by

\[
N_s! \equiv (N_s - N_H)!
\]

Thus, the partial entropy of a solute atom is given by

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Ideal case:

\[ S_c = -k \ln \left( \frac{N_H}{N_s - N_H} \right) \quad (e) \]

where eq e is essentially the same as eq a.

However, experimental fact shows that hydrogen atoms cannot be closer than 0.21 nm, therefore case 5 is not allowed (in this example, the distance 0.21 nm corresponds to two sites): i.e., the blocking effect must act even at lower concentration according to experimental fact. We need to exclude case 5 from eq d. Thus, the concept of SBM that the blocking effect is negligible at lower concentration is not realistic. There is a discrepancy between experimental fact and the concept of SBM. SBM needs to exclude case 5 in this situation.

A schematic representation of the SOM (site-occupying model) at low concentration is shown in Figure 3 as an example. My idea is to assign two sites (\( \zeta = 2 \)) for one hydrogen atom. Atom B can be located in 2 ways: cases 1 and 2. The number of locatable cases in SOM decreases from 5 (the ideal case) to 2.

Equation d is rewritten as follows:

\[ \text{SOM:} \]

\[ \frac{N_s!}{\zeta!} \left( \frac{N_s}{\zeta} - N_H \right)! \quad (d') \]

Thus, eq e is rewritten as follows:

\[ S_c = -k \ln \left( \frac{N_H}{N_s - N_H} \right) \quad (e') \]

where eq e' is essentially the same as eq c.

In my paper, I actually counted the number of \( \zeta \) for the three lattices, fcc, hcp, and bcc. The values of \( \zeta \) are listed in Table 1 in my paper.²

As a result of this decrease (5 to 2), the curve of SOM shows a negative deviation compared to those of the ideal case and SBM in Figure 1. Figure 1 corresponds to Figure 10 on page 2142 in my paper.²

My paper shows that the theoretical curve of SOM with eq c (eq 15 on page 2138 in my paper²) agrees well with experimental values compared to those of SBM even at high hydrogen concentration of over 0.5 H/M: this result is shown in Figures 2–8 in my paper.²

References and Notes