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# Johnson-Mehl-Avrami-Kolmogorov model applied to describe the site blocking effect in interstitial solid solution

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## Abstract

Interstitial solid solutions, such as carbon in steels or hydrogen in metal and alloys, are important materials for many applications. Thermodynamic models that accurately predict the behavior of interstitial solid solution are essential for designing new materials and to improve computational materials tools. In this work, we revisited the problem of calculating the configurational entropy of interstitial solid solutions when site blocking effect occurs. Using an unprecedented approach, we propose a new site blocking model that uses the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation to calculate the fraction of blocked sites. Since the occupation of interstitial sites in solid solutions is random, the blocking of neighbor sites can also be assumed to be random. Thus, the blocking site effect can be described as a Poisson process and the JMAK equation can be derived from Poisson statistics. The proposed model (to be called JMAK model) allows to estimate the number of blocked sites considering the site blocking overlapping phenomenon in a simple and direct way. The JMAK model was validated by comparing the calculated values of configurational entropy with both numerical simulation and experimental data.

**Keywords:** interstitial solid solution, configurational entropy, site blocking effect, Johnson-Mehl-Avrami-Kolmogorov model.

# 1 Introduction

Interstitial atoms play important roles in different areas of materials science and engineering. Many properties are governed and/or affected by the the formation of interstitial solid solution. Carbon in steel is the typical example of how interstitial atoms can affect the mechanical properties of metals and alloys. Hydrogen storage in metals and metal hydrides is another example of interstitial atoms playing a central role in the materials properties. In the era of computational materials science, thermodynamic models that can accurately describe the behavior of interstitial solid solution is paramount to boost the design of new materials.

The configurational entropy of interstitial solid solutions often deviates from the ideal entropy of mixing because of short-range repulsion of two interstitial atoms. In this case, when an atom occupies a random interstitial site, some of its interstitial site neighbors will become unavailable for receiving another interstitial atom because of the repulsive forces. Therefore, these unavailable (or blocked) sites can no longer participate in the mixing process, affecting the number of possible atomic configurations. This phenomenon is called site blocking effect (SBE) and has been discussed in literature for more than 60 years and many authors reported theoretical or empirical models to calculate the configurational entropy of interstitial solid solution when SBE occurs [1–6].

In this work, we revisited this problem and derived a general expression to calculate the configurational entropy for interstitial solid solutions with SBE, which is only function of the fraction of occupied and blocked sites. Moreover, we propose a new model to describe the fraction of blocked sites, which uses the well-known Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation and that we called JMAK model. It is worth mentioning that the JMAK equation has already been applied to describe different physical phenomena in materials science and beyond, such as in biochemical processes, genetics studies, ecology, epidemiology, social studies, product market analysis, and others [7, 8].

Since the interstitial occupation occurs as a random and independent process, we supposed that the distribution of blocked sites is also a random and independent process. Therefore, the Poisson process with the phantom nuclei and extended volume concepts should be suitable for describing the site blocking phenomena and obtain the JMAK equation [9]. Furthermore, we demonstrated that the JMAK equation is a simple and straightforward way to account for the site blocking overlapping, i.e., when one site can be simultaneously blocked by the previous occupation of two or more neighbor sites. The JMAK model proposed here was confronted with both numerical simulation and experimental data, as well as with other site blocking models reported in literature. The SBE effect of tetrahedral sites in body-centered cubic (BCC) lattice with different levels of blocking was simulated using open code written in Python language. Furthermore, experimental pressure-composition-temperature (PCT) diagrams of the V-H, Nb-H, and Ta-H systems reported in [10] were used to extract the partial molar configurational entropy for the hydrogen interstitial solid solution for the three metals. The JMAK model presented here describes well both the simulated and experimental results, accurately predicting the fraction of blocked sites for different levels of blocking in interstitial solid solutions.

## 2 Theory

### 2.1 Configurational entropy of interstitial solid solution with site blocking effect

In this session, we will derive the general expression for configurational entropy of an interstitial solid solution when SBE occurs.

Let  $N$  be the total number of interstitial sites in a metal lattice. Then:

$$N = n_i + n_v + n_b \quad (1)$$

where  $n_i$  is the number of sites occupied by an interstitial specie  $i$ ,  $n_v$  is the number of vacant sites, and  $n_b$  is the number of blocked sites. Therefore,

$$\frac{n_i}{N} + \frac{n_v}{N} + \frac{n_b}{N} = f_i + f_v + f_b = 1 \quad (2)$$

where  $f_i$  is the fraction of sites occupied by an interstitial specie  $i$ ,  $f_v$  is the fraction of vacant sites, and  $f_b$  is the fraction of blocked sites.

The configurational entropy of an interstitial solid solution can be described by considering only the interstitial species and vacancies, which are the only ‘‘species’’ that can mix between them. In other words, the blocked sites do not participate in the mixing process. Therefore:

$$\frac{S_c}{k} = -N' [P_i \ln P_i + P_v \ln P_v] \quad (3)$$

where  $N'$  is the quantity of sites that can mix and need to be accounted for the different possible configurations, i.e., the quantity of sites excluding the blocked sites ( $N(1 - f_b)$ ).  $P_i$  and  $P_v$  are, respectively, the probability of finding an occupied and an available site among the  $N'$  sites. Then:

$$\frac{S_c}{k} = -N(1 - f_b) \left[ \frac{f_i}{1 - f_b} \ln \left( \frac{f_i}{1 - f_b} \right) + \frac{1 - f_b - f_i}{1 - f_b} \ln \left( \frac{1 - f_b - f_i}{1 - f_b} \right) \right] \quad (4)$$

For convenience, we can describe the quantity of interstitial sites ( $N$ ) in terms the number of interstitial sites per metal atom ( $\theta$ ), as follow:

$$N = n_M \cdot \theta \quad (5)$$

where  $n_M$  is the the number of moles of metal atoms in the lattice. Then, the configurational entropy for the solid solution per mol of metal atom is given by:

$$\frac{S_c}{R} = -\theta \cdot (1 - f_b) \cdot \left[ \frac{f_i}{1 - f_b} \ln \left( \frac{f_i}{1 - f_b} \right) + \frac{1 - f_b - f_i}{1 - f_b} \ln \left( \frac{1 - f_b - f_i}{1 - f_b} \right) \right] \quad (6)$$

It is worth noting that the concentration of interstitial atoms ( $c_i$ ) is given by:

$$c_i = \frac{n_i}{n_M} = f_i \cdot \theta \quad (7)$$

Finally, we can derive the general expression of the partial molar configurational entropy ( $\overline{S}_c$ ), as follow:

$$\overline{S}_c = \frac{\partial S_c}{\partial c_i} = \frac{1}{\theta} \frac{\partial S_c}{\partial f_i} = -R \ln \left( \frac{f_i (1 - f_b)^{\frac{\partial f_b}{\partial f_i}}}{(1 - f_i - f_b)^{1 + \frac{\partial f_b}{\partial f_i}}} \right) \quad (8)$$

## 2.2 Site blocking models: Introduction of the JMAK model for SBE

Given the general expression for the configurational entropy of interstitial solid solutions with SBE, equation 6, one need to know how the fraction of blocked sites varies with  $f_i$ .

J. Garcés [5] reported a model to describe the configurational entropy of interstitial solid solutions with SBE following the same general expression described above. In his work, it was considered that the fraction of blocked sites varies linearly with the fraction of occupied sites as follow:

$$f_b = N_b \cdot f_i \quad (9)$$

where  $N_b$  is the number of neighbor interstitial sites that are blocked by the previous occupation of an interstitial site.

The problem concerning Garcés model is that it does not consider the overlapping of blocked sites. This scenario is depicted in Figure 1 for a 2D square lattice with one interstitial site in the center of the lattice, and with blocking of the first and second near neighbor (NN) interstitial sites. Figure 1 (a) shows that when two random sites far apart from each other are occupied, all the first and second NN sites are blocked. However, Figure 1 (b) shows that when a random site near to the already blocked site is occupied, the blocked sites are overlapped. For the Garcés model, the number of blocked sites in Figure 1 (b) would be 16, while in reality the number of blocked sites is only 14. One can imagine that when the fraction of occupied sites increases, the number of overlapped sites also becomes more important. As a result of not considering the site blocking overlapping, the maximum fraction of interstitial species allowed for the solid solution is reduced, since the blocked sites will be overestimated. In this case, the maximum solubility of an interstitial specie would be underestimated.

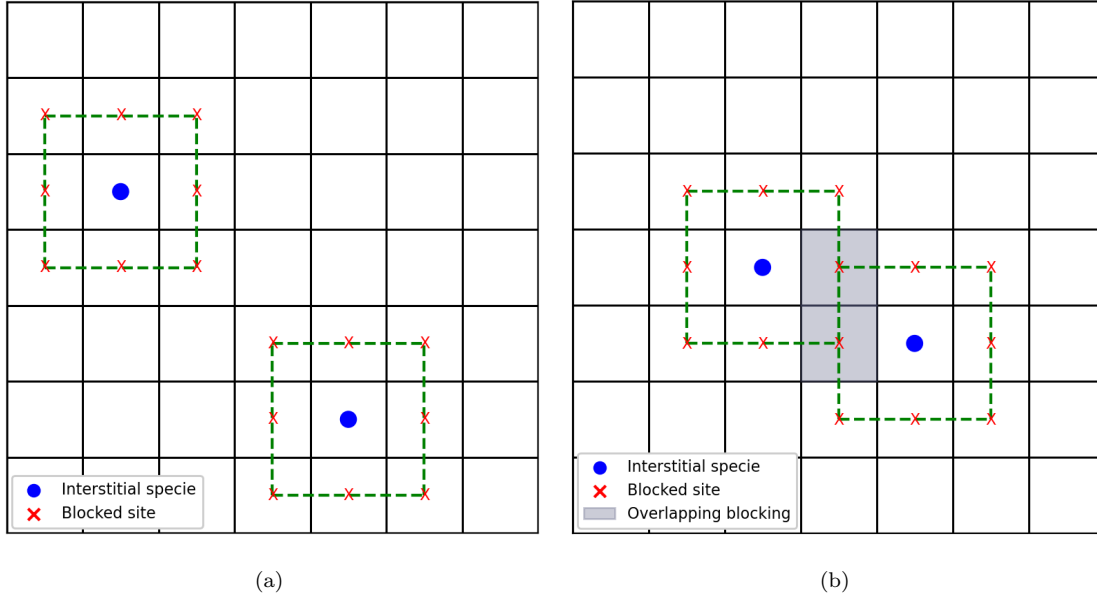


Figure 1: 2D square lattice with one interstitial site in the center of the unit cell with SBE taking place by blocking the first and second NN interstitial sites. (a) Occupation of two interstitial sites far apart from each other, resulting in a total number of blocked sites of 16. (b) Occupation of two interstitial sites near from each other, resulting in a total number of 14 blocked sites because of the overlapping.

The idea behind the site block overlapping is not new, and has been discussed in 1967 by McLellan et al. [2], who proposed an empirical expression to include the overlap of blocked sites. In his model, the partial molar configurational entropy is given by:

$$\overline{S}_c = -\ln \frac{\theta}{1 - Z'\theta + X\theta^2} \quad (10)$$

where  $Z'$  and  $X$  are empirically determined constants. This site blocking model was further modified by Gallagher, Lambert, and Oates [3] who introduced a composition-dependent  $Z'$ .

In 1980, G. Bureau proposed a simple method to calculate the configurational entropy of interstitial solid solution when SBE occurs [4]. The author states that the  $\overline{S}_c$  may be calculated from the relationship:

$$\overline{S}_c = \ln \frac{g(c_i)}{c_i} \quad (11)$$

Through statistical analyses, G. Bureau derived the  $g(c_i)$  equations for the tetrahedral sites in BCC interstitial solutions when the first, first and second, first, second and third near interstitial site neighbors are blocked, yielding equations 12, 13, and 14: respectively:

$$g(c_i) = \frac{z(c_i + z)}{6}; z = \frac{(6 - 2c_i)(72 - 36c_i + 5c_i^2)}{2(6 - c_i)^2} \quad (12)$$

$$g(c_i) = \frac{(6 - 4c_i)^2}{6 - c_i} \quad (13)$$

$$g(c_i) = \frac{(6 - 5c_i)^4(6 - 4c_i)}{(6 - 2c_i)^3(6 - 3c_i)} \quad (14)$$

In this work, we present a completely new approach of how to describe the SBE in interstitial solid solutions. We analyzed this problem by making an analogy to the total extended volume of transformed phase ( $V^*$ ) from the well-known Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [7], typically used to describe phase transformation phenomena in metallurgy.  $V^*$  represents the total relative volume of transformed phase (related to a unit volume of the starting parent phase) that all the crystals taken together might have occupied, if they had had the chance to grow free, and if their overlapping with the neighboring grains in the space and blocking of each other had been neglected. In the JMAK model, the actual volume of transformed phase ( $V$ ) relates to  $V^*$  by:

$$V = 1 - \exp(-V^*) \quad (15)$$

$V^*$  can be described generally by  $V^* = K(T)(t - t_0)^n$ , where  $K(T)$  is a nucleation and growth dependent prefactor in function of the temperature  $T$ ,  $t$  is the observation time,  $t_0$  is the initial nucleation time, and  $n$  is the Avrami exponent related to the kinds of phenomena of nucleation and growth. The Avrami exponent can be described as  $n = n_{nucleation} + d \cdot n_{growth}$  [7], where  $n_{nucleation} = 1$  for constant nucleation and  $n_{nucleation} = 0$  for no nucleation,  $d$  is the dimension of growth, and  $n_{growth} = 1$  for interface controlled and  $n_{growth} = 0.5$  for diffusion controlled growth. Then, different exponents can be found depending on the phenomena and boundary conditions of the system during the phase transformation, such as  $n = 1$  when there is a constant nucleation rate with no growth, and  $n = 2$  for constant nucleation rate and diffusion controlled in 2 dimensional growth. More detailed derivations and examples of the JMAK model can be found in [7].

Although the SBE phenomenon discussed here is very different from the phase transformation kinetic phenomenon described by the JMAK model, we propose that the same idea behind the  $V^*$  can be used to describe the fraction of blocked sites of random interstitial solid solutions. We define here the concept of extended fraction of blocked sites ( $f_b^*$ ), which represents the total number of blocked sites if the overlapping of blocked sites is neglected. Analogously, the actual fraction of blocked sites is given by the JMAK equation, as follow:

$$f_b = 1 - \exp(-f_b^*) \quad (16)$$

As proposed,  $f_b^*$  can be seen as an analogue of  $V^*$ , i.e., should follow the same kind of equation. However, different from the extended volume, the extended fraction of occupied sites should not be time dependent, but composition dependent, which is directly related to the fraction of occupied sites  $f_i$ , as  $f_b^* = K(f_i, T)(f_i)^n$ , where the prefactor  $K$  should depend in the composition and temperature. In this way, we assume that the blocking site effect is an analogue process of a phase transformation with a constant nucleation rate without growth. Since there is no growth,  $K(f_i, T) \equiv K(f_i) \propto N_b$ . Thus, we propose that  $N_b \cdot f_i$ , which is the Gárces model, actually describes  $f_b^*$  instead of  $f_b$ . Thus:

$$f_b = 1 - \exp(-N_b \cdot f_i) \quad (17)$$

It is important mentioning that the JMAK equation was initially derived from a statistical analysis of the phase transformation problem assuming the random nucleation of the new phase in a Poisson process. In the next section, we will show that equation 17 can also be derived from the Poisson distribution statistics.

### 3 Site blocking effect as Poisson Process and its Relationship with JMAK Model

The distribution of interstitial species in  $N$  interstitial sites in an interstitial solid solution is a random process. If each interstitial specie blocks  $N_b$  near site neighbors, the distribution of the blocked sites is also random. Therefore, the distribution of blocked sites can be regarded as a Poisson process, i.e., a process where certain events occur at a constant rate, but at random and independently of each other.

Typically, the Poisson process is a time dependent statistic. However, for our problem we have a spatial Poisson process which is described by the equation:

$$P(X(S) = k) = \frac{(\lambda A(S))^k e^{-\lambda A(S)}}{k!} \quad (18)$$

where  $S$  is a delimited region,  $\lambda$  is the average number of events per volume,  $A(S)$  is the volume of the region  $S$ , and  $X(S)$  is the number of events inside  $S$ . In our problem, we can look each site a time since all interstitial sites are equal, so we can delimit a region  $S$  that contains one interstitial site, where for each occupation fraction  $f_i$  there is an intensity parameter of  $\lambda = N_b \cdot f_i$  to the site be blocked, which is related to the quantity of blocked sites per quantity of interstitial species. Then, to determine the probability of a site be blocked, we need to calculate the probability of do not find the interstitial site blocked,  $k = 0$ . Through equation 19, one can obtain:

$$P(X(S) = 0) \equiv P_0 = e^{-N_b \cdot f_i} \quad (19)$$

Finally, the probability to find a site blocked is:

$$P_b(f_i) = 1 - P_0(f_i) = 1 - \exp(-N_b f_i) \quad (20)$$

which is the JMAK equation for SBE. Remarking the occupation and the blocking effect occurs randomly and independently for all sites, the probability to find a site blocked is equivalent to the fraction of blocked sites.

To demonstrate the validity of the JMAK model for SBE, we will present in the next section a numerical simulation that allowed to determine the fraction of blocked sites when SBE is taking place in tetrahedral sites of BCC interstitial solid solutions.



## 4 Numerical simulation of SBE

Using Python language, we carried out a numerical simulation for a BCC lattice with 12 tetrahedral interstitial sites per unit cell considering three blocking conditions:

- i) blocking of the 1st NN sites ( $N_b = 4$ );
- ii) blocking of 1st and 2nd NN sites ( $N_b = 6$ );
- iii) blocking of the 1st, 2nd, and 3rd NN sites ( $N_b = 14$ ).

For each of these three scenarios, the numerical simulation was carried out as follows:

- 1) A BCC lattice with approximately 250,000 interstitial sites was generated (27x27x28 unit cells).
- 2) Then, a random interstitial site was picked to be filled with an interstitial specie using the NumPy `random.randint` function.
- 3) A new lattice is generated by removing both the occupied site and the NN blocked sites from the original lattice, resulting in a new lattice of “available sites”. In addition, lattices of “occupied sites” and of “blocked sites” are also generated. Then, the fraction of occupied, vacant, and blocked sites is counted.
- 4) Next, another random interstitial site is picked from this new lattice of “available sites” and the whole process is repeated until no more available sites exist.

The code for these numerical simulations is available in [github.com/oapedroso/JMAK\\_model](https://github.com/oapedroso/JMAK_model).

Figures 2 (a), (c), and (e) present the simulated values of  $f_b$  for  $N_b = 4, 6,$  and  $14$ , respectively, compared to those calculated by the Garcés and JMAK models. One can see that for very low values of  $f_i$ , i.e., for very diluted solid solutions, the Garcés model accurately predicts the fraction of blocked sites, since for diluted solid solutions blocking overlapping is a less important event. However, when  $f_i$  increases, the simulated values of  $f_b$  considerably deviate from the Garcés model because site blocking overlapping becomes more likely. Thus, for non-diluted solid solutions, the Garcés model strongly overestimates the fraction of blocked sites. The JMAK model proposed here takes the site blocking overlapping into account, resulting in a behavior of  $f_b$  in function of  $f_i$  very close to the simulated ones, regardless the value of  $N_b$ . Although the calculated values of  $f_b$  using the JMAK model were not identical to the simulated ones, the JMAK model could reasonably predict the fraction of blocked sites when blocking overlapping occurs. This results in a better description of the configurational entropy of the interstitial solid solutions with SBE, as can be seen in Figures 2 (b), (d), and (f). Whereas the Garcés model underestimates the maximum solubility of the solid solutions (because of the overestimation of blocked sites) and leads to maximum configurational entropies lower than the simulated ones, the JMAK model could better describe both the maximum solubility and the maximum configurational entropy for the different levels of blocking for the BCC solid solutions.

Thus, we believe that the JMAK model presented here is a simple and direct model to describe configurational entropy of interstitial solid solutions when SBE occurs. In the next section, the experimental data of PCT diagrams of different metal-hydrogen systems will be analyzed and compared with the different site blocking models.

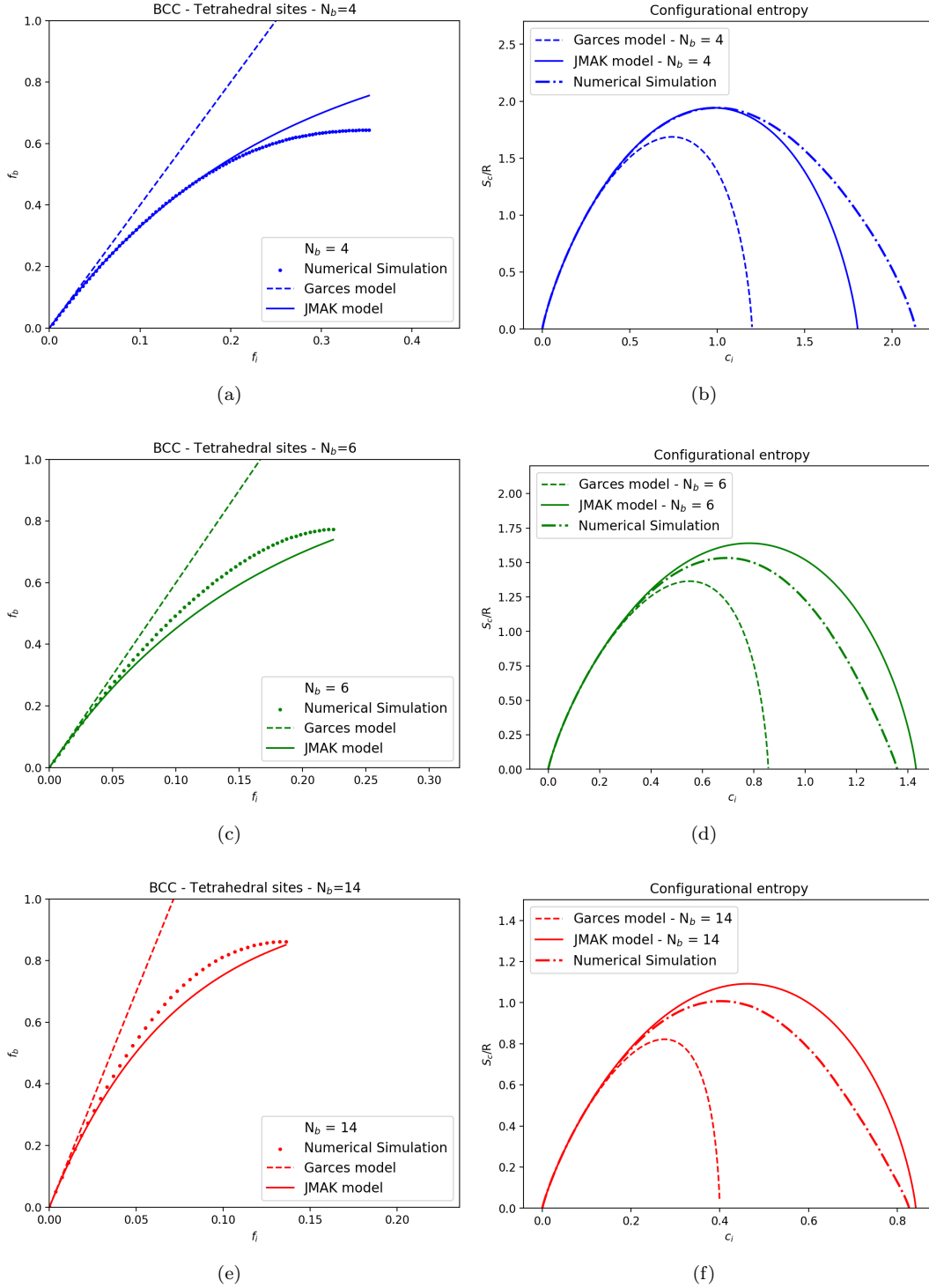


Figure 2: Comparison of  $f_b$  and  $S_c$  obtained by numerical simulation, Garcés Model, and JMAK model for (a) and (b)  $N_b = 4$ ; (c) and (d)  $N_b = 6$ ; and (e) and (f)  $N_b = 14$ . Numerical Simulation of a BCC lattice with approximately 250.000 tetrahedral interstitial sites.

## 5 Comparison with Experimental Data: Hydrogen in BCC Metals

Many BCC metals and alloys can absorb large amounts of hydrogen by interstitial solid solution. V, Nb, and Ta are typical examples of BCC metals studied for hydrogen storage applications. For V, Nb, and Ta, at low hydrogen pressure, the interstitial solid solution ( $\alpha$  phase) is the only phase in thermodynamic equilibrium with the hydrogen gas. For each metal, the hydrogen concentration in the  $\alpha$  phase depends on both  $H_2$  pressure and temperature. Careful studies performed in the 1960s' by neutron diffraction and reported in [11], showed the hydrogen occupies the tetrahedral sites in the BCC lattice of the  $\alpha$  phase for the three metals. It is well established and accepted the rule that states that H atoms do not come closer than 2.1 Å, due to the short-range repulsion between two hydrogen atoms [12]. For the tetrahedral sites in a BCC lattice, the distances of the first, second, and third neighbors in respect to one interstitial site are  $a\sqrt{2}/4$ ,  $a/2$ , and  $a\sqrt{6}/4$ , respectively, where  $a$  is the lattice parameter. Figure 3 shows how these distances vary with the lattice parameter. The lattice parameters of V, Nb, and Ta are 3.031 Å [13], 3.301 Å [13], and 3.302 Å [13], respectively. Therefore, by analyzing Figure 3 and considering the minimum distance between two hydrogen atoms, we conclude that for V, Nb, and Ta  $N_b$  must be equal to 14.

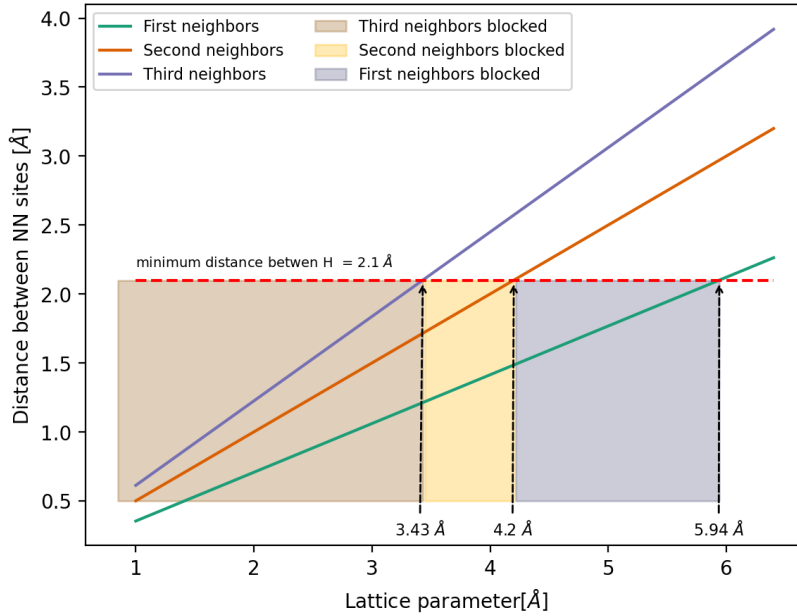
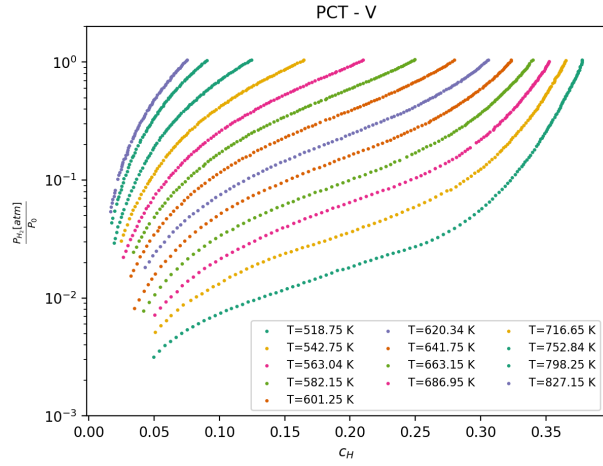
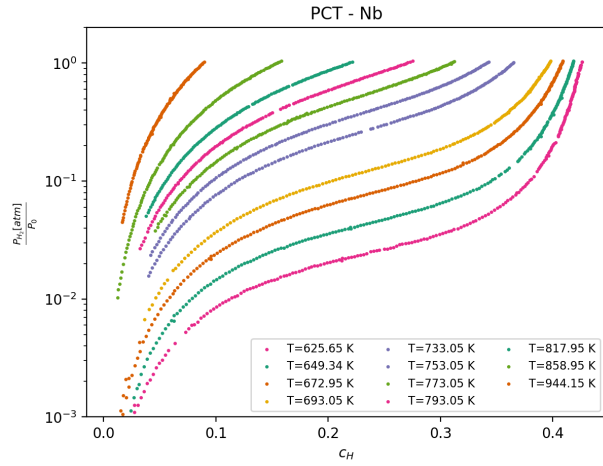


Figure 3: Distance between first, second, and third neighbor sites of the tetrahedral sites in a BCC lattice as function of lattice parameter.

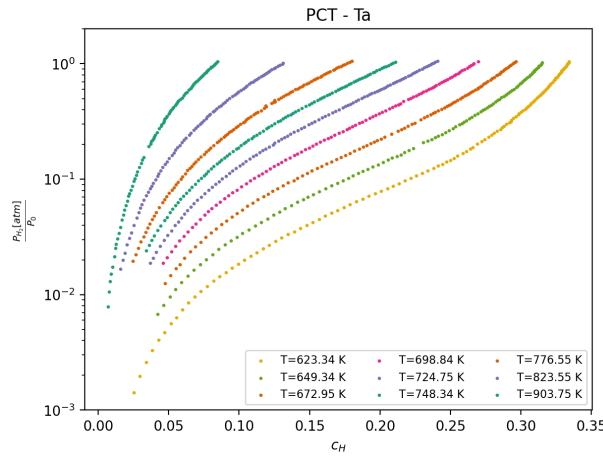
E. Veleckis and R. K. Edwards [10] reported the experimental PCT diagrams for low hydrogen pressures for V, Nb, and Ta, whose data are presented in Figure 4.



(a)



(b)



(c)

Figure 4: Experimental Pressure-Composition-Temperature diagrams for V, Nb, and Ta. Data extracted from [10].

From the PCT diagrams, we can extract the experimental values of the partial molar configurational entropy of the V-H, Nb-H, Ta-H solid solutions as follow.

For the hydrogen gas and the  $\alpha$  phase to be in equilibrium, their hydrogen chemical potential must be the same:

$$\mu_H^g = \mu_H^\alpha \quad (21)$$

The chemical potential of the hydrogen gas per mol of H atom is given by:

$$\mu_H^g = RT \frac{1}{2} \ln \left( \frac{P_{H_2}}{P_0} \right) \quad (22)$$

where R is the universal gas constant, T is the absolute temperature, and  $P_0 = 1$  atm is the standard hydrogen pressure.

The hydrogen chemical potential of the  $\alpha$  phase is defined as:

$$\mu^\alpha(c_H) = \frac{\partial \Delta G^\alpha(c_H)}{\partial c_H} = \overline{\Delta H^\alpha}(c_H) - T \overline{\Delta S^\alpha}(c_H) \quad (23)$$

where  $\Delta G^\alpha(c_H)$  is the variation of the Gibbs free energy between the  $\alpha$  phase with hydrogen concentration  $c_H$  and the standard state, i.e., the pure metal and hydrogen gas at  $P_0$ .  $\overline{\Delta H^\alpha}(c_H) = \frac{\partial \Delta H^\alpha(c_H)}{\partial c_H}$  and  $\overline{\Delta S^\alpha}(c_H) = \frac{\partial \Delta S^\alpha(c_H)}{\partial c_H}$  are the hydrogen partial molar enthalpy and entropy of the  $\alpha$  phase, respectively,

Therefore, under equilibrium conditions:

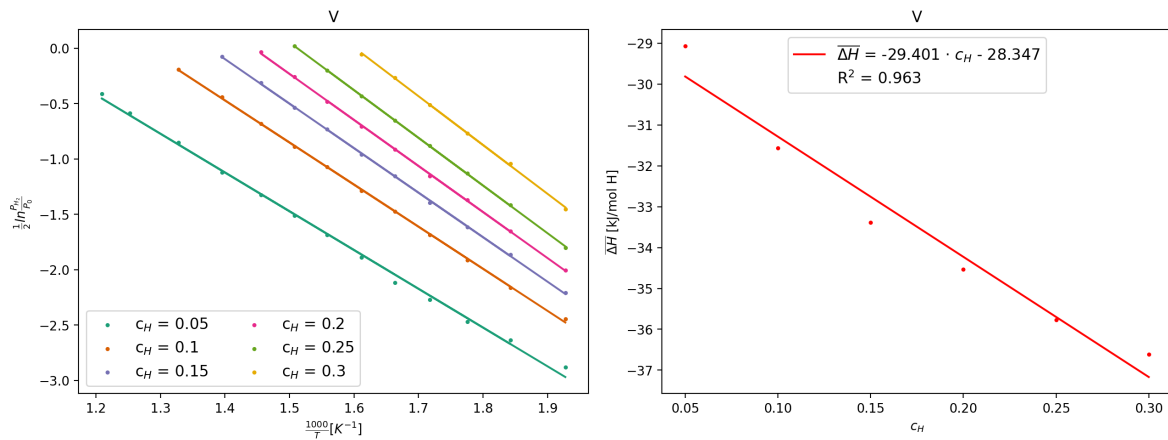
$$\frac{1}{2} \ln \left( \frac{P_{H_2}}{P_0} \right) = \frac{\overline{\Delta H^\alpha}(c_H)}{RT} - \frac{\overline{\Delta S^\alpha}(c_H)}{R} \quad (24)$$

$\overline{\Delta H^\alpha}(c_H)$  can be found by the linearization of  $\frac{1}{2} \ln \left( \frac{P_{H_2}}{P_0} \right)$  versus  $1/T$  for the different values of  $c_H$ , as presented in Figures 5 (a), (b), and (c), for V, Nb, and Ta, respectively. Figure 5 also shows that  $\overline{\Delta H^\alpha}$  varies almost linearly with  $c_H$ . By linear regression, we found the following equations for  $\overline{\Delta H^\alpha}$  for V, Nb, and Ta:

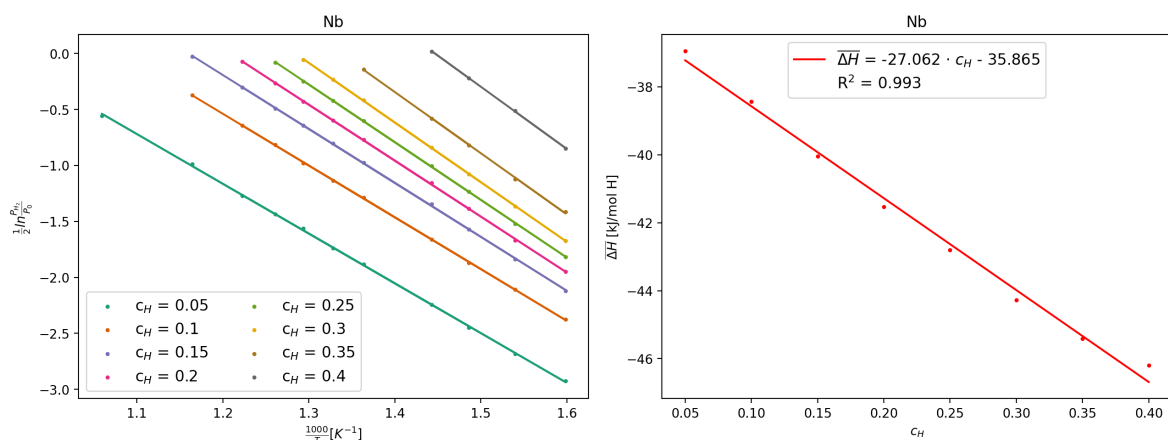
$$V : \overline{\Delta H^\alpha}(c_H) = -29.401 \cdot c_H - 28.347 \quad (25)$$

$$Nb : \overline{\Delta H^\alpha}(c_H) = -27.062 \cdot c_H - 35.865 \quad (26)$$

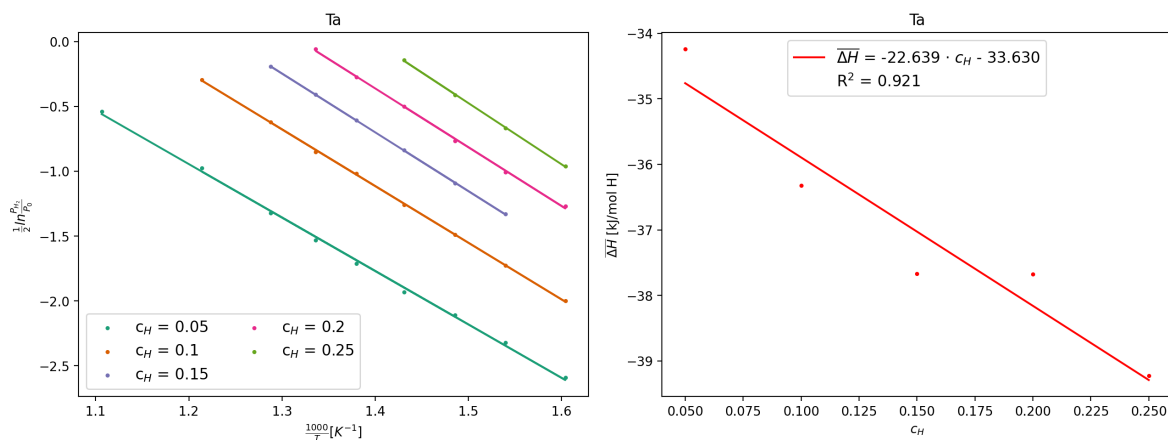
$$Ta : \overline{\Delta H^\alpha}(c_H) = -22.639 \cdot c_H - 33.630 \quad (27)$$



(a)



(b)



(c)

Figure 5: Linearization of  $\frac{1}{2} \ln \left( \frac{P_{H_2}}{P_0} \right)$  versus  $1/T$  for the different values of  $c_H$  for (a) V, (b) Nb, and (c) Ta.

$\Delta S^\alpha(c_H)$  is the entropy variation between the  $\alpha$  phase with hydrogen concentration  $c_H$  and the standard state, therefore:

$$\Delta S^\alpha(c_H) = S^\alpha(c_H) - S^M(c_H) - \frac{c_H}{2} S_{H_2}^0 \quad (28)$$

where  $S^\alpha(c_H)$  is the entropy of the  $\alpha$  phase with  $c_H$  composition,  $S^M$  is the entropy of the pure metal, and  $S_{H_2}^0$  is the standard entropy of hydrogen gas given by equation 29 according to [14].

$$S^0(H_2) = A \ln(t) + Bt + \frac{Ct^2}{2} + \frac{Dt^3}{3} + \frac{Et^{-2}}{2} + G \quad (29)$$

where  $t = T \text{ [K]}/1000$ ,  $A = 33.066178$ ,  $B = -11.363417$ ,  $C = 11.432816$ ,  $D = -2.772874$ ,  $E = -0.158558$ , and  $G = 172.707974$ . This equation is only valid between 298 K and 1000 K [14].

If we consider that the difference between the non-configurational entropy of the  $\alpha$  phase and the pure metal is very small and, therefore, can be neglected, then:

$$\Delta S^\alpha(c_H) = S_c^\alpha(c_H) - \frac{c_H}{2} S_{H_2}^0 \quad (30)$$

and,

$$\overline{\Delta S^\alpha}(c_H) = \overline{S_c^\alpha}(c_H) - \frac{1}{2} S_{H_2}^0 \quad (31)$$

Substituting equation 31 into equation 24, the partial molar configurational entropy of the  $\alpha$  phase can be determined by:

$$\overline{S_c^\alpha} = \frac{\overline{\Delta H^\alpha}(c_H)}{T} - \frac{R}{2} \ln\left(\frac{P_{eq}}{P_0}\right) + \frac{1}{2} S_{H_2}^0 \quad (32)$$

Figure 6 presents  $\overline{S_c^\alpha}$  for V, Nb, and Ta derived from the experimental data using equation 32. It is worth noting that data from all measured temperatures is presented in these curves. The experimental values of  $\overline{S_c^\alpha}$  is compared to those calculated using the Gárces, Boureau, and JMAK models. As already reported by J. Gárces [5] in his work, the partial molar configurational entropy of V, Nb, and Ta solid solutions is better describe by his model when  $N_b = 6$  is considered. However, as previous discussed here,  $N_b = 6$  does not respect the minimum distance of 2.1 Å between two hydrogen atoms. For the Gárces model, when  $N_b = 14$  is considered, the maximum solubility of H in V, Nb, and Ta is underestimated because the fraction of blocked sites is overestimated, resulting in a deviation between the experimental and calculated  $\overline{S_c^\alpha}$ . The Boureau model can reasonably describe the values of  $\overline{S_c^\alpha}$  when both  $N_b = 6$  and  $N_b = 14$  is considered. However, in both cases, the maximum hydrogen solubility in the  $\alpha$  phase seems to be overestimated. The JMAK model presented here accurately describe the values of  $\overline{S_c^\alpha}$  when  $N_b = 14$  is considered, resulting in a maximum hydrogen solubility in V, Nb, and Ta of about  $c_H = 0.84$ . Interestingly, this value agrees with the number of sites available for hydrogen occupation in V, Nb, and Ta experimentally determined by E. Veleckis and R.K. Edwards [10], which were 0.779, 0.904, and 0.702, respectively.

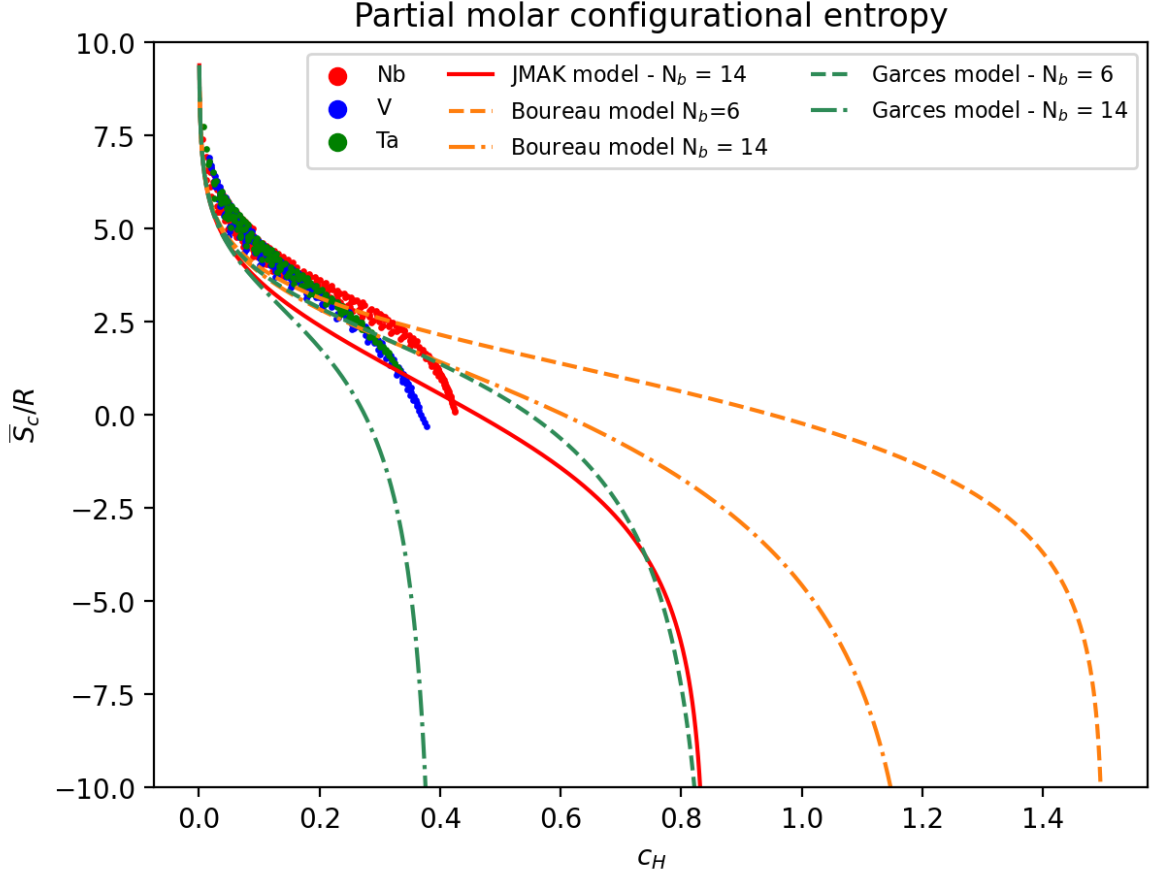


Figure 6: Comparison between experimental values of partial molar configurational entropy for V, Nb, and Ta, and those calculated by the JMAK model ( $N_b = 14$ ), Gárces model ( $N_b = 6$  and  $14$ ) and Boureau model ( $N_b = 6$  and  $14$ ).

## 6 Conclusions

In this work, we derived a general expression for calculating the configurational entropy of interstitial solid solutions with site blocking effect. In addition, we proposed a new site blocking model (JMAK), in which the Johnson-Mehl-Avrami-Kolmogorov equation is applied to describe the fraction of blocked sites as function of the fraction of occupied sites. The JMAK equation is a simple and straightforward way to take into account the site blocking overlapping. Using numerical simulation, we demonstrate that the JMAK model is the best description so far of the fraction of blocked sites for different levels of blocking in tetrahedral sites in BCC lattice. Experimental pressure-composition-temperature diagrams of the V-H, Nb-H, Ta-H systems were used to extract experimental values of the partial molar configurational entropy of the interstitial solid solutions for the three metals. There was a good agreement between the experimental and calculated values using the JMAK. Moreover, the JMAK model accurately predicted the maximum number of sites available for hydrogen occupation



for V, Nb, and Ta, which was experimentally determined by E. Veleckis and R.K. Edwards [10]. The JMAK model is a simple and effective model to describe the configurational entropy of interstitial solid solution when SBE occurs and can be applied to many materials science related problems.

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