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The influence of the ideal mixing entropy on concentration profiles and diffusion paths in ternary systems

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Abstract

The diffusion profiles and the reaction paths in ternary solid solutions are determined by both thermodynamics and kinetics. The matrix of the diffusion coefficient can be described as the product of the Hessian matrix for the thermodynamic influences and the Onsager matrix for kinetic influences.

In this paper the interest is focused on the influence of the ideal part of the Hessian matrix, i.e. the ideal mixing entropy on interdiffusion. The ideal diffusion profiles are calculated by a computer simulation and they are compared with experimental results from the literature. These comparisons reveal that in most cases the qualitative shape of the diffusion profiles and of the reaction paths can be considered as caused by the ideal mixing entropy. Surprisingly the shape of the diffusion profiles turns out to depend on the component that was chosen as the so-called solvent of the ternary mixture. This means that the ideal reaction paths do not show the triangular symmetry expected for an ideal ternary system. Especially reaction paths between starting positions showing the same concentration of one of the three components do not run along straight lines.

Keywords: Interdiffusion; Ternary systems; Thermodynamics; Computer simulation;

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1 Introduction

By definition ternary systems are systems in which the composition can be described by two independent variables and the diffusion by a 2x2 diffusion matrix. Diffusion paths $k(l)$ in ternary systems of type $A_kB_lC_m$ with $k + l + m = 1$ are calculated from two mole fraction profiles e.g. $k(z)$ and $l(z)$ by eliminating the space coordinate z for diffusion in one dimension. These mole fraction profiles are usually measured by an electron microprobe or they can be determined from computer simulations realized by solving the diffusion equations with a finite difference algorithm. [1, 2].

The matrix $\mathbf{D}$ of the diffusion coefficients can be written as the product of the Onsager matrix $\mathbf{L}$ and of the Hessian matrix $\mathbf{M}$ of the Gibbs free energy [3, 4]. In matrix notation one obtains:

$$\mathbf{D} = \frac{1}{C} (\mathbf{L} \cdot \mathbf{M}) \quad (1)$$

C is here a scalar, namely the mean molar concentration of the components.

The Onsager matrix considers the mobility part of the diffusion matrix, whereas the Hessian matrix describes the thermodynamic contribution to the diffusion process. Generally it is paid much too little attention to the contribution of the Hessian matrix and in the literature in some cases the Hessian matrix is even not correctly formulated. Therefore we will discuss in this paper the influence of the Hessian matrix in a thermodynamically ideal system on the diffusion profiles of ternary systems. For this purpose the Onsager matrix will be taken as a scalar and all thermodynamic interaction parameters as zero.

2 Theoretical considerations

2.1 The Onsager matrix $\mathbf{L}$

In a ternary system $A_kB_lC_m$ with two independent mole fractions the flux of each component $i \in \{A, B, C\}$ is principally a linear function of the driving forces X_i [5]:

$$\begin{aligned} J_A &= l_{AA}X_A + l_{AB}X_B + l_{AC}X_C \\ J_B &= l_{BA}X_A + l_{BB}X_B + l_{BC}X_C \\ J_C &= l_{CA}X_A + l_{CB}X_B + l_{CC}X_C, \end{aligned} \quad (2)$$

but, because of $\sum_i J_i = 0$, these fluxes are not independent. To get a description with independent fluxes and forces we have to reduce this equation

system by taking one component - being called the solvent [6] - as depending on the others. Choosing C as the solvent we obtain [6, 5]:

$$\begin{aligned} J_A &= L_{AA}^C(X_A - X_C) + L_{AB}^C(X_B - X_C) \\ J_B &= L_{BA}^C(X_A - X_C) + L_{BB}^C(X_B - X_C) \end{aligned} \quad (3)$$

Depending on the component that was chosen as solvent the matrices describing these equation systems are:

$$\left| \begin{array}{cc} L_{AA}^C & L_{AB}^C \\ L_{BA}^C & L_{BB}^C \end{array} \right| \quad \left| \begin{array}{cc} L_{BB}^A & L_{BC}^A \\ L_{CB}^A & L_{CC}^A \end{array} \right| \quad \left| \begin{array}{cc} L_{CC}^B & L_{CA}^B \\ L_{AC}^B & L_{AA}^B \end{array} \right| \quad (4)$$

The upper indices indicate, which component was chosen as the solvent.

The term solvent is only a conventional designation for that component whose composition was chosen as depending on those of the other two components. It is used for the whole system covering all compositions including even such compositions, where this 'solvent' is the minor component.

The Onsager coefficients l_{ij} of the equation system (2) can be described as functions of the new Onsager coefficients L_{ij} in the matrices (4) [5]. As the reduced 2x2 matrices belong to equation systems with independent fluxes and independent forces, the coefficients L_{ij} can take any values, provided the restrictions $L_{ii} \geq 0$, $L_{jj} \geq 0$, $L_{ii}L_{jj} \geq 1/4(L_{ij} + L_{ji})$ [7] and the Onsager relations $L_{ij} = L_{ji}$ [8] are considered.

As our principal object in this paper will be to show the influence of thermodynamics on diffusion processes, we will simplify the Onsager matrices (4) as scalar, i.e. we will take the off diagonal elements as zero and all diagonal elements as constant and equal. Thus, such an Onsager matrix $\mathbf{L}$ will only affect the length of the diffusion profiles, but not the shape of the diffusion path.

2.2 The ideal mixing term of the Hessian matrix M

To calculate the elements of the Hessian matrix for a ternary system of type $A_k B_l C_m$ we need the mean molar Gibbs energy g as a function of two independent mole fractions, e.g. k and l . The Gibbs energy

$$g = k\mu_A + l\mu_B + m\mu_C \quad (5)$$

can be split in the standard term g^0 , the ideal mixing term g^{id} and the excess term g^{E} :

$$g = g^0 + g^{\text{id}} + g^{\text{E}} \quad \rightarrow \quad \mathbf{M} = (\mathbf{M}^0 + \mathbf{M}^{\text{id}} + \mathbf{M}^{\text{E}}) . \quad (6)$$

With component C as solvent we have to take the mole fractions k and l of the components A and B as the independent variables. Considering that $k + l + m = 1$ it follows from eq.(5) that

$$\frac{\partial g}{\partial k} = \mu_A - \mu_C = \mu_{A-C} \quad \frac{\partial g}{\partial l} = \mu_B - \mu_C = \mu_{B-C} \quad (7)$$

These are the chemical potentials of the difference building units (A-C) and (B-C) describing the exchange of a solvent atom C for one of the independent components A or B. The negative gradients of the chemical potentials of these building units are the independent forces according to eq.(3). The partial differentials of these chemical potentials with respect to the independent variables k or l are the second derivatives of the mean molar Gibbs energy, i.e. the elements of the Hessian matrix with C as solvent:

$$\frac{\partial \mu_{A-C}}{\partial k} = \frac{\partial^2 g}{\partial k^2} = M_{kk}^C, \quad \frac{\partial \mu_{A-C}}{\partial l} = \frac{\partial^2 g}{\partial k \partial l} = M_{kl}^C, \quad (8)$$

$$\frac{\partial \mu_{B-C}}{\partial l} = \frac{\partial^2 g}{\partial l^2} = M_{ll}^C, \quad \frac{\partial \mu_{B-C}}{\partial k} = \frac{\partial^2 g}{\partial l \partial k} = M_{lk}^C. \quad (9)$$

As the chemical standard potentials of the pure components are independent of composition, the standard term $\mathbf{M}^0$ vanishes, but nevertheless also in thermodynamically ideal systems the three components are still energetically different. The ideal mixing term g^{id} is restricted to the ideal mixing entropy, because the ideal mixing enthalpy is zero per definition.

$$g^{\text{id}} = -T s^{\text{id}} = RT \cdot \ln [k^k \cdot l^l \cdot m^m] \quad \text{with} \quad m = 1 - k - l. \quad (10)$$

Thus, for k and l as the independent variables, the elements of the ideal mixing term $\mathbf{M}^{\text{id}}$ of the Hessian matrix become

$$M_{kk}^{C,\text{id}} = RT \left(\frac{1}{k} + \frac{1}{m} \right), \quad M_{ll}^{C,\text{id}} = RT \left(\frac{1}{l} + \frac{1}{m} \right), \quad M_{kl}^{C,\text{id}} = M_{lk}^{C,\text{id}} = RT \cdot \frac{1}{m}. \quad (11)$$

It is astonishing that in the literature relevant to this subject [3] the elements of the ideal mixing term of the Hessian matrix are given as

$$M_{kk}^{C,\text{id}} = RT \left(\frac{1}{k} \right), \quad M_{ll}^{C,\text{id}} = RT \left(\frac{1}{l} \right), \quad M_{kl}^{C,\text{id}} = M_{lk}^{C,\text{id}} = 0. \quad (12)$$

The reason for this error is probably that, in differentiating the chemical potentials $\bar{\mu}_{ij} = \partial(\mu_i - \mu_C)/\partial x_j$ with $i, j \in \{A, B\}$, it was not considered that the chemical potential $\mu_C = \mu_C^0 + RT \ln m$ of the dependent component C depends also on the mole fraction k and l via $m = 1 - k - l$.

The appearing of the term $1/m$ in eq.(11) has severe consequences. This term effects that even in ideal mixtures a thermodynamic coupling of fluxes occurs because of $M_{kl}^{C,\text{id}} = M_{lk}^{C,\text{id}} \neq 0$. Moreover, also the diagonal elements of the Hessian matrix depend on $1/m$.

If - as in developing eq.(11) - the mole fractions k and l of the components A and B were chosen as the independent variables, the component C belonging to the mole fraction $m = 1 - k - l$ is called - as already mentioned above - the solvent of this ternary system. The superscript C in eq.(11) means that for this case C was chosen as the solvent. The corresponding cases for the solvents A and B read as follows:

$$M_{ll}^{A,\text{id}} = RT \left(\frac{1}{l} + \frac{1}{k} \right), \quad M_{mm}^{A,\text{id}} = RT \left(\frac{1}{m} + \frac{1}{k} \right), \quad M_{lm}^{A,\text{id}} = M_{ml}^{X,\text{id}} = RT \cdot \frac{1}{k}. \quad (13)$$

$$M_{mm}^{B,\text{id}} = RT \left(\frac{1}{m} + \frac{1}{l} \right), \quad M_{kk}^{B,\text{id}} = RT \left(\frac{1}{k} + \frac{1}{l} \right), \quad M_{mk}^{B,\text{id}} = M_{km}^{Y,\text{id}} = RT \cdot \frac{1}{l}. \quad (14)$$

In order that calculated mole fraction profiles or diffusion paths for ideal systems were independent of the choice of the solvent, both the determinant and the trace of the ideal Hessian matrix would have to be invariant with respect to the choice of the solvent S [6]. The determinants d^S of the matrices with the elements of eqs.(11),(13) or (14) are indeed invariant:

$$d^A = d^B = d^C = \frac{1}{k \cdot l \cdot m}, \quad (15)$$

but their traces are not invariant. Thus the simulation of mole fraction profiles and diffusion paths in ideal ternary systems must yield different results for different choices of the solvent.

By the way, for the wrong matrices corresponding to eq.(12) neither the determinants nor the traces are invariant with respect to the solvent choice, and therefore mole fraction profiles calculated on this basis would also have to depend on the choice of the solvent.

The usual expectation that diffusion paths in ternary ideal systems would run along straight lines is generally not true and the statement that in an ideal solution all elements of the diffusion matrix reduce to the purely kinetic form $D_{ij} = RT L_{ij} / x_j$ [9] does not hold either. Instead we have to consider that even in ideal systems the Hessian matrix is not diagonal and that their off-diagonal elements, $M_{ij}^{S,\text{id}}$ with $(i \neq j)$, must always depend on composition (eq.11,13,14).

Whereas the function g^{id} (eq.10) shows the threefold symmetry of the Gibbs triangle, the matrix of its second derivatives (eq.11) does not so. Thus,

the whole field of possible reaction paths in the thermodynamically ideal system does not yield the expected triangular symmetry, but only a mirror symmetry related to the line $x = y$ for the case that x and y are chosen as the independent mole fractions. Moreover, the simulation of reaction paths for thermodynamically ideal ternary triangular systems shows that no reaction path yields a straight line except the path for the reaction between the component chosen as solvent and the equimolar mixture of the other two components.

3 Comparison of calculated diffusion profiles with experiments from the literature

3.1 Cu-Ag-Au

Fig.1a shows the phase diagram with the miscibility gap at 1000 K for the system $\text{Cu}_k\text{Ag}_l\text{Au}_m$ according to Ziebold and Ogilvie [10]. This figure contains a series of diffusion paths. For comparison we have calculated these diffusion paths for the ideal system $\text{X}_k\text{Y}_l\text{Z}_m$ as shown in Fig.1c,d. Fig.1c belongs to Z as solvent and Fig.1d to X as solvent. One can clearly see that the shapes of these calculated diffusion paths depend on the solvent choice. Comparing the calculated diffusion paths starting at pure X or Y with the experimental ones starting at Cu or Ag, one can see that the diffusion paths of Fig.1c correspond qualitatively much better with the experimental paths in Fig.1a than those of Fig.1d. For the two diffusion paths with the starting points $(l = 0, m = 0.55)$ and $(k = 0, m = 0.45)$ or $(l = 0, m = 0.55)$ and $(k = 0, m = 0.7)$ one cannot decide so easily, because these calculated diffusion paths for the two solvent cases differ only quantitatively but not qualitatively. Nevertheless, it looks rather clear that in the system Cu-Ag-Au the component Au acts as solvent. This result is consistent with the experience that in ternary systems with a spinodal miscibility gap near the edge XY [4] the component on the corner Z opposite to the miscibility gap acts most probably as solvent.

Though the given system deviates from the thermodynamically ideal behavior so much that it forms even at 1000 K a spinodal miscibility gap, one can understand the qualitative shape of the diffusion paths just from the ideal mixing entropy without considering an influence of the Onsager matrix or any interaction parameters for real systems.

The diffusion paths starting with one of the pure components show the well known S-shaped course, i.e. they cross the straight line joining the two starting points of the path only one time and their Au profiles (cf.Fig.1b)

Figure 1: (a) Experimental diffusion paths and the miscibility gap at 1000 K in the system Cu-Ag-Au (After [10]). (b) The calculated mole fraction profiles of Au with the same starting compositions as the diffusion paths in (a), but for a thermodynamically ideally behaving system $\text{Cu}_k\text{Ag}_l\text{Au}_m$ with Au as solvent. (c) Calculated diffusion paths for a thermodynamically ideally behaving system X-Y-Z for Z and (d) for X as solvent.

don't show any region of uphill diffusion.

The two paths in Fig.1c between $(l = 0, m = 0.55)$ and $(k = 0, m = 0.45)$ or between $(l = 0, m = 0.55)$ and $(k = 0, m = 0.7)$, however, cross the straight line between the two starting points two times. Such a behaviour was until now seldom experimentally observed [11], but the computer simulations of diffusion paths for an ideal system show that this is a usual behavior for diffusion couples with about equal starting content of the solvent component in both partners of the couple. Fig.1b shows the calculated m -profiles for the diffusion paths of Fig.1c. In the profiles for the diffusion path between $(l = 0, m = 0.55)$ and $(k = 0, m = 0.7)$ (Fig.1b) the Au flux runs from right to left including two regions of uphill diffusion (the path regions with negative slope). In experiments the tiny minima at the ends of the diffusion path can easily be overlooked, because they correspond in the Au profile to the two

extended regions with very slowly changing Au concentrations outside the two shallow minima of the profile. This could be the reason for the missing minimum on the left side of the corresponding experimental reaction path in Fig.1a.

In the diffusion path between $(l = 0, m = 0.55)$ and $(k = 0.55, m = 0.45)$ and in the m profile we have an equivalent situation, but now the Au flux runs from left to right.

3.2 Ni-Co-Fe

Figure 2: (a) Experimentally determined mole fraction profiles for Co and Ni in the system Ni-Co-Fe (after [12]); (b) Calculated profiles with the same starting compositions as in (a), but for the thermodynamically ideally behaving system with Fe as solvent.

Interdiffusion processes in the system Ni-Co-Fe were experimentally intensively investigated by Vignes and Sabatier [12]. Fig.2a shows the Ni and Co profiles for one of the many diffusion paths they had measured. By Kirkaldy and Young [13] this system was taken as a thermodynamically ideal solution with Fe as solvent and it was '*emphasized that the diffusion interactions are of entirely kinetic origin*'. As we have already shown in [4] this is wrong, because already the influence of the ideal mixing entropy suffices to explain the qualitative behaviour of the experimentally determined diffusion paths. Thus, one cannot say that the redistribution of Ni is '*due primarily to the diffusional cross-effect represented by D_{12}* ' [13]. The redistribution is rather a thermodynamic effect, caused by the ideal mixing entropy as shown in Fig.2b. Moreover one must not set $D_{21} = 0$, because the off-diagonal elements of the Hessian matrix are equal and do not vanish even in thermodynamically ideal systems ($M_{12}^{id} = M_{21}^{id} \neq 0$, eq.(11,13,14)).

Thus, the diffusion behaviour in the system Ni-Co-Fe is predominantly determined by thermodynamics, namely by the ideal part of the Hessian matrix (Eq.11). For example, for the diffusion couple shown in Fig.2, the computer simulations of the mole fraction profiles for a thermodynamically ideal system - even with the scalar Onsager matrix - yield the experimentally observed redistribution of Ni. The assumption in the literature that in this system Fe acts as solvent was confirmed by our computer simulations.

3.3 Cu-Ni-Zn

Figure 3: (a) Mole fraction profiles for Cu, Ni and Zn in the system Cu-Ni-Zn (after Dayananda [14]); (b) The calculated profiles for the thermodynamically ideally behaving system with the same starting positions as in (a) and with Zn as solvent.

Fig.3a shows the mole fraction profiles measured by Dayananda in the system Cu-Ni-Zn at about 1000 K. The Ni profile is characterized by a light uphill diffusion. If the profiles of the three components are calculated by computer simulation for a thermodynamically ideal system, the region of clear uphill diffusion for the Ni profile can only be reproduced if the component Zn is chosen as solvent. For Ni as solvent one gets only a very tiny maximum in the Ni profile, and for Cu as solvent there is not at all any uphill diffusion for Ni.

These results reveal that the shape of the calculated reaction paths depends on which component was chosen as solvent and that by comparison of the calculated and experimentally determined profiles one can decide which component acts really as solvent.

Figure 4: (a) and (c): Mole fraction profiles for Fe, Al and Ni in the system Fe-Al-Ni (after [15]); (b) and (d): The calculated profiles with the same starting positions as in (a) and (c) for the thermodynamically ideally behaving system with Al as solvent.

3.4 Fe-Al-Ni

Some diffusion paths within the ordered β_2 -phase of the system Fe-Al-Ni were investigated by Moyer and Dayananda [15]. The left plots in Fig.4 show the experimentally determined mole fraction profiles of these diffusion paths. The right plots show the mole fraction profiles of all three components Fe, Al and Ni calculated using a scalar Onsager matrix and the assumption of a thermodynamically ideal solution with Al chosen as solvent. Figs.4a,b belong to a diffusion path with the same Al content and Fig.4c,d to one with the same Fe content in both starting compositions. For such situations in ideally behaving systems it is usually expected that the diffusion paths yield straight lines between the starting points, i.e. the Al profile in Fig.4b and the Fe profile in 4d would then have to be straight lines. But both, the experimentally determined and the calculated profiles show distinctly a redistribution of Al or Fe by the diffusion process. Al in Fig.4a,b diffuses from the right to the left side, Fe in Fig.4c,d, however from the left to the

right side. In Fig.4d the calculated redistribution is much weaker than the experimentally measured one. Nevertheless, the computer simulations of the mole fraction profiles yield - in spite of the restrictive assumptions - qualitatively the same results as the experiments of Moyer and Dayananda [15].

4 Discussion

The calculations have shown that, if the full ideal part of the Hessian matrix (eq.11) is considered, the shape of a diffusion path depends on the choice of the solvent. Until now, we do not know how one could predict from physical arguments which of the three components acts really as solvent. However, by comparing the calculated mole fraction profiles or diffusion paths with the experimental data we can determine, which component has to be chosen as solvent. Kirkaldy has already written - with regard to the discussion of diffusion coefficients in ternary systems - that '*the choice of solvent is by no means a trivial matter*' [6].

Figure 5: (a) Calculated k and l profiles for the reaction between $M(X_{0.5}Y_{0.5})$ and $N(X_{0.5}Y_{0.5})$ at 1000 K in a thermodynamically ideal system $(M_kN_{1-k})(X_lY_{1-l})$ with a standard Gibbs energy of the reaction $MX + NY \rightarrow NX + MY$ of $\Delta_r G^0 = +20 \text{ kJ/mol}$. (b) The diffusion path calculated from the profiles in (a).

If in an ideal ternary system all three components could be taken as identical, the thermodynamic properties must not depend on the arrangement of the three components, i.e. the collectivity of the diffusion paths should obey the triangular symmetry of the phase triangle independent of the solvent choice. But, generally the three components are not identical. They still differ energetically by their chemical standard potentials μ_i^0 , and therefore

it is possible that an exchange of two pure components - or equivalently a change of the independent variables - will influence the shape of the reaction paths.

Such an influence of the chemical nature of the components on the behaviour of ideal mixtures can also be detected for quasiternary systems of type $(M_k N_{1-k})(X_l Y_{1-l})$, in which all four quasibinary subsystems $(M_k N_{1-k})X$, $(M_k N_{1-k})Y$, $M(X_l Y_{1-l})$ and $N(X_l Y_{1-l})$ behave ideally. In these cases the essential diffusion paths also don't run along straight lines (cf. Fig.5b). Really, one could assume that in this ideal square system the shape of the diffusion paths would have to obey a mirror symmetry, i.e. an exchange of M for N or of X for Y should have no influence on the shape of the reaction paths. But Fig.5b reveals that reflecting the diffusion path at $l = 0.5$ or at $k = 0.5$ yields new diffusion paths.

The Hessian matrix of such an ideal quasiternary system reads :

$$M_{11}^{id} = RT \frac{1}{k(1-k)}, \quad M_{12}^{id} = M_{21}^{id} = -\Delta_R G^0, \quad M_{22}^{id} = RT \frac{1}{l(1-l)} \quad (16)$$

In contrast to this formulation the off-diagonal elements of the ideal matrix are generally taken as zero [1], and $\Delta_R G^0$ is then treated as part of the off-diagonal elements of the excess term. But, as $\Delta_R G^0 = \sum \nu_i \mu_i^0$, this term does not vanish in ideal systems, and as it only depends on the standard chemical potentials of the components of the reaction (R), $MX + NY \rightarrow NX + MY$ [16, 17], it can alternatively be identified with the off-diagonal elements of the ideal part of the Hessian matrix. That means that, even in thermodynamically ideal systems, the shape of the diffusion path must change, if the chemical nature of the components changes. The uphill diffusion, shown by the l -profile in Fig.5a, is caused by the thermodynamic coupling because of the off-diagonal elements of the Hessian matrix.

Similarly the role of the solvent in ideal triangular systems could depend on the values of the standard chemical potentials of the components, and if this is the case, the choice of the independent composition variables or of the component acting as solvent is not at our free disposal. Moreover, if one describes a reaction path $l(k)$ of a ternary triangular system in a rectangular Cartesian coordinate system with the composition of the solvent at its origin, the mirror symmetry related to the diagonal $k = l$ for an ideal system is reasonable, but one is not automatically obliged to look also for a triangular symmetry.

5 Summary

The comparisons of the experimental mole fraction profiles for extended solid solutions in ternary systems with the profiles determined by computer simulations for the same starting compositions show that most probably the qualitative behaviour of many experimental profiles and diffusion paths is essentially determined by the ideal mixing entropy of the solid solution.

Especially we could show by the computer simulations that the usually expected quasibinary sections, i.e. straight lines for the reaction paths, in thermodynamically nearly ideal mixtures do generally not occur. The single exception is the diffusion path between the component being chosen as solvent and the equimolar mixture of the other two components of the ternary system [4].

Thus, I think that, for the interpretation of diffusion profiles and reaction paths in ternary systems, it is essential to consider the influence of the ideal mixing entropy. The simulation of diffusion profiles and reaction paths for thermodynamically ideal conditions can yield valuable information on the qualitative behaviour of the diffusion process. In cases, where it is known which component acts as solvent - as for example in systems with a spinodal miscibility gap detected at lower temperatures - the reaction paths for nearly ideal systems can in many cases qualitatively be predicted by the computer simulation, even if the diffusion coefficients are not known.

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