On Negative Diagonal Elements in the Diffusion Coefficient Matrix of Multicomponent Systems

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Abstract In multicomponent systems the diffusion coefficient turns into a matrix. The diagonal elements represent diffusion of a species caused by its own concentration gradient. In a thermodynamically stable binary alloy it is easy to see that this diagonal element must be positive but in a multicomponent system it is less obvious. The sign of the diagonal elements in the general case is discussed in this report. It is shown that the sign of an individual diagonal element has no physical meaning but can be changed by changing the dependent concentration variable. Only the sum of all the diagonal elements need to be positive in a stable system.

Keywords Fick–Onsager law · thermodynamics · Onsager relations · mobility

1 Introduction

In the simplest case diffusion of a species may be represented by Fick’s law but in systems with many components it is replaced by the so-called Fick–Onsager law.^[1] The

latter is a vector-matrix equation and the single diffusion coefficient of Fick’s law now turns into a matrix. In a thermodynamically stable binary alloy the diffusion coefficient must be positive. In a multicomponent system the diagonal elements of the diffusion coefficient matrix represent diffusion of a species caused by its own concentration gradient. The purpose of the present discussion is to discuss the sign of the diagonal elements in the general case.

2 Fick–Onsager Law

Fick’s law is readily extended to any number of components. It becomes particularly simple to make the extension when vector-matrix notation is used and we write the Fick–Onsager law as

$$J = -D\nabla C \quad (\text{Eq 1})$$

J is the column vector that contains the fluxes J_i as components, i.e. the transported amount of i expressed per unit area and unit time in the direction of the concentration gradient ∇C which is the column vector containing the gradients of all the concentrations c_i , i.e. the amount i per unit volume. The amount is usually expressed as mole and c_i is then related to the mole fraction x_i by $c_i = x_i/V_m$, where V_m is the molar volume. D is the $N \times N$ matrix containing the diffusivities D_{ij} . In the classical Fick’s law all its elements, except the diagonal ones are zero, but Eq 1 allows for general matrices.

In early experimental investigations of ternary diffusion couples negative diagonal coefficients were found, see for example the study by Akuezue and Stringer.^[2] However, the negative value was quite small and they concluded that

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it should have no significance and was within the experimental error. Obviously they felt uncomfortable with the negative value. Much earlier Kirkaldy^[3] had investigated various constraints on the elements of D both on a thermodynamic and kinetic basis. However, he was not able to show that individual diagonal elements were required to be positive. Castleman^[4] was intrigued by what he regarded as inconclusive results of Kirkaldy and performed an analysis showing that thermodynamics did not require that individual diagonal elements needed to be positive. Unfortunately, his analysis is quite cumbersome and the purpose of the present paper is to show this result in a simpler and hopefully more transparent way.

In this discussion we will essentially follow the analysis by Andersson and Ågren,^[5] which is the basis for the DICTRA software, although we shall use matrix-vector notation which makes the algebra simpler. The reader may try this approach using softwares like Maple^{TM}.

3 Practical Diffusion Coefficients

The diffusion coefficients used in practical calculations and their values depend on what frame of reference is used and which concentration gradient that is considered as dependent. Since the N concentrations are not independent one gradient may be eliminated and consequently one column in the D matrix can be eliminated so it may be written as an $N \times (N - 1)$ matrix. However, it may be convenient to keep it as an $N \times N$ matrix and simply let the column corresponding to the dependent concentration variable only contain zeros. If the molar volume is approximated as constant and we eliminate the N th concentration gradient the diffusion coefficients become

$$D_{kj}^N = D_{kj} - D_{kN} \quad (\text{Eq 2})$$

The diffusion coefficient also depends on the frame of reference. In a crystalline material one may use the crystalline lattice as reference, the lattice-fixed frame of reference. These diffusion coefficients are often referred to as intrinsic or individual diffusion coefficients. The N fluxes are independent in the lattice-fixed frame of reference, i.e. there is no way to calculate one of the fluxes if one knows the $N - 1$ other fluxes. Practical calculations are often based on the number-fixed frame of reference where the flux J_i is defined in such a way that

$$\sum_{i=1}^N J_i = 0 \quad (\text{Eq 3})$$

Transformation from the lattice-fixed frame of reference to the number-fixed frame is achieved by multiplying the fluxes with an $N \times N$ transformation matrix A . The

diffusion coefficient matrix is transformed by the same matrix, i.e.

$$D' = AD \quad (\text{Eq 4})$$

The A matrix has the elements $a_{ik} = \delta_{ik} - x_i$, where δ_{ik} is the Kronecker delta and is unity when $i = k$ and zero otherwise. However, as one flux is superfluous one replaces one row in A with another combination of the fluxes. One such combination is the sum $\sum_{i=1}^N J_i$ which is non-zero when fluxes are given the lattice-fixed frame. In fact, it represents the net-flow of atoms relative the lattice and is related to the migration velocity v_K of Kirkendall markers expressed in the number-fixed frame.

$$v_K/V_m = - \sum_{i=1}^N J_i \quad (\text{Eq 5})$$

i.e.

$$A = \begin{bmatrix} 1 - x_1 & -x_1 & \dots & -x_1 \\ -x_2 & 1 - x_2 & \dots & -x_2 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \dots & 1 \end{bmatrix} \quad (\text{Eq 6})$$

The N th flux thus is $J'_N = -v_K/V_m$, i.e. proportional to Kirkendall velocity expressed in the number-fixed frame.

It must be emphasized that Eq 4 also holds for the matrix D^N where the N th concentration gradient has been eliminated and one column only contains zeros.

4 Diffusion Coefficients Based on Thermodynamic Driving Forces

In the linear theory of irreversible thermodynamics isothermal diffusion of a species k is written in terms of the gradient in chemical potentials $\nabla \mu_k$ and a matrix L called the phenomenological matrix. Equation 1 thus is replaced by

$$J = -L \nabla \mu \quad (\text{Eq 7})$$

In this case the second law of thermodynamics ensures that L must be positive definite. Moreover, the Onsager reciprocity relations ensure that it is symmetric. It is common to assume that L is a diagonal matrix when diffusion is expressed in the lattice-fixed frame of reference and so-called correlation effects are neglected. In fact that assumption is supported by modelling based on the so-called vacancy mechanism and a random solution. In this case L is symmetric in a trivial case, i.e. its N diagonal elements must all be positive.

When the L -matrix and the functions $\mu_k(x_1, x_2, \dots)$ are known one may calculate the diffusion coefficients of

interest. We may start with the formulation in the lattice-fixed frame of reference i.e. Eq 7, with the driving forces $\nabla\mu_k$ which may be expanded in the concentration gradients as

$$\nabla\mu = \frac{d\mu}{dX} V_m \nabla C \quad (\text{Eq 8})$$

where it is assumed that the molar volume V_m is constant. The matrix $d\mu/dX$ is

$$\frac{d\mu}{dX} = \begin{bmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \dots & \frac{\partial\mu_1}{\partial x_N} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \dots & \frac{\partial\mu_2}{\partial x_N} \\ \vdots & \vdots & \ddots & \vdots \end{bmatrix} \quad (\text{Eq 9})$$

In all partial derivatives pressure and temperature are kept constant. Equation 7 thus transforms into

$$J = -V_m L \frac{d\mu}{dX} \nabla C \quad (\text{Eq 10})$$

Comparing with Eq 1 we thus identify

$$D = V_m L \frac{d\mu}{dX} \quad (\text{Eq 11})$$

The diffusion coefficient matrix D in the lattice-fixed frame of reference thus is the product of two matrices, one purely kinetic L and one thermodynamic $d\mu/dX$, usually referred to as the thermodynamic factor and calculated from the CALPHAD databases. The L matrix is calculated from the mobility databases.

5 The Requirements of Thermodynamic Stability

Thermodynamic stability is discussed in the textbook by Hillert.^[6] It is evident that it requires that the matrix $d\Phi/dX$ with elements $\partial\Phi_i/\partial x_j = \partial(\mu_i - \mu_N)/\partial x_j$ has a positive determinant and positive eigenvalues. Since it is symmetric it is thus positive definite. N is an arbitrarily chosen reference element. In the number-fixed frame of reference the thermodynamically conjugate driving forces to the flux are precisely $\nabla\Phi$ and the corresponding L matrix is denoted L' and given by $L' = ALA^T$. Equation 10 and 11 then become

$$J' = -V_m L' \frac{d\Phi}{dX} \nabla C \quad (\text{Eq 12})$$

and we may identify

$$D' = V_m L' \frac{d\Phi}{dX} \quad (\text{Eq 13})$$

Here it is clear that both $d\Phi/dX$ and L' are symmetric and positive definite and consequently, D' is the product of two symmetric and positive definite matrices, and according to matrix algebra it should have real and positive eigenvalues although it is not necessarily symmetrical or positive definite.

The fact that all eigenvalues are real and positive gives an important property involving the diagonal coefficients. The sum of the diagonal elements D' is the first invariant of matrix D' , i.e. it must also be the sum of D' 's eigenvalues λ_i . If they are all positive then

$$\text{Tr}D' = \sum_{i=1}^N D'_{ii} = \sum_{i=1}^N \lambda_i > 0 \quad (\text{Eq 14})$$

6 Ternary Systems

We shall now demonstrate an example of negative diagonal coefficients for a ternary system. In the case when L is diagonal Eq 11 yields

$$D = V_m \begin{bmatrix} L_{11} \frac{\partial\mu_1}{\partial x_1} & L_{11} \frac{\partial\mu_1}{\partial x_2} & L_{11} \frac{\partial\mu_1}{\partial x_3} \\ L_{22} \frac{\partial\mu_2}{\partial x_1} & L_{22} \frac{\partial\mu_2}{\partial x_2} & L_{22} \frac{\partial\mu_2}{\partial x_3} \\ L_{33} \frac{\partial\mu_3}{\partial x_1} & L_{33} \frac{\partial\mu_3}{\partial x_2} & L_{33} \frac{\partial\mu_3}{\partial x_3} \end{bmatrix} \quad (\text{Eq 15})$$

Taking x_3 as dependent and applying Eq 2 remembering that μ_k does not depend on x_3 , i.e. $\partial\mu_k/\partial x_3 = 0$, we obtain,

$$D^3 = V_m \begin{bmatrix} L_{11} \frac{\partial\mu_1}{\partial x_1} & L_{11} \frac{\partial\mu_1}{\partial x_2} & 0 \\ L_{22} \frac{\partial\mu_2}{\partial x_1} & L_{22} \frac{\partial\mu_2}{\partial x_2} & 0 \\ L_{33} \frac{\partial\mu_3}{\partial x_1} & L_{33} \frac{\partial\mu_3}{\partial x_2} & 0 \end{bmatrix} \quad (\text{Eq 16})$$

Transforming to number-fixed frame of reference, i.e. Eq 4, one obtains

$$D'^3 = V_m \begin{bmatrix} (1-x_1)L_{11}\frac{\partial\mu_1}{\partial x_1} - x_1L_{22}\frac{\partial\mu_2}{\partial x_1} - x_1L_{33}\frac{\partial\mu_3}{\partial x_1} & (1-x_1)L_{11}\frac{\partial\mu_1}{\partial x_2} - x_1L_{22}\frac{\partial\mu_2}{\partial x_2} - x_1L_{33}\frac{\partial\mu_3}{\partial x_2} & 0 \\ -x_2L_{11}\frac{\partial\mu_1}{\partial x_1} + (1-x_2)L_{22}\frac{\partial\mu_2}{\partial x_1} - x_2L_{33}\frac{\partial\mu_3}{\partial x_1} & -x_2L_{11}\frac{\partial\mu_1}{\partial x_2} + (1-x_2)L_{22}\frac{\partial\mu_2}{\partial x_2} - x_2L_{33}\frac{\partial\mu_3}{\partial x_2} & 0 \\ -L_{11}\frac{\partial\mu_1}{\partial x_1} - L_{22}\frac{\partial\mu_2}{\partial x_1} - L_{33}\frac{\partial\mu_3}{\partial x_1} & -L_{11}\frac{\partial\mu_1}{\partial x_2} - L_{22}\frac{\partial\mu_2}{\partial x_2} - L_{33}\frac{\partial\mu_3}{\partial x_2} & 0 \end{bmatrix} \quad (\text{Eq 17})$$

It is common to define the reduced diffusivity matrix as the $(N-1) \times (N-1)$ matrix obtained by removing the “ N ”th column and row, i.e.

7 Ideal Solution or Dilute Solutions

In an ideal solution there are no thermodynamic interactions between the species. Most real systems are far from

$$D'_{red}{}^3 = V_m \begin{bmatrix} (1-x_1)L_{11}\frac{\partial\mu_1}{\partial x_1} - x_1L_{22}\frac{\partial\mu_2}{\partial x_1} - x_1L_{33}\frac{\partial\mu_3}{\partial x_1} & (1-x_1)L_{11}\frac{\partial\mu_1}{\partial x_2} - x_1L_{22}\frac{\partial\mu_2}{\partial x_2} - x_1L_{33}\frac{\partial\mu_3}{\partial x_2} \\ -x_2L_{11}\frac{\partial\mu_1}{\partial x_1} + (1-x_2)L_{22}\frac{\partial\mu_2}{\partial x_1} - x_2L_{33}\frac{\partial\mu_3}{\partial x_1} & -x_2L_{11}\frac{\partial\mu_1}{\partial x_2} + (1-x_2)L_{22}\frac{\partial\mu_2}{\partial x_2} - x_2L_{33}\frac{\partial\mu_3}{\partial x_2} \end{bmatrix} \quad (\text{Eq 18})$$

It may be shown that Eq 17 and 18 give the same result as Eq 13. In this case the focus is on the sign of D'_{11} and D'_{22} in the original matrix or the reduced matrix. For example, consider D'_{22} and a case where L_{22} and L_{33} are both very small. In that case

$$D'_{22} \cong -V_m x_2 L_{11} \frac{\partial\mu_1}{\partial x_2} \quad (\text{Eq 19})$$

If $\partial\mu_1/\partial x_2 > 0$ this coefficient is clearly negative because the three L -parameters are always positive, although they can be small. This would happen if species 2 lowers the chemical potential of species 1, not an unusual situation. It has thus been shown that certain combinations of phenomenological parameters and thermodynamic interactions may lead to negative diagonal diffusivities.

It should be emphasized that the fact a certain diagonal diffusivity is negative has no physical significance and if one chooses another species as dependent and look at e.g. D'^2 the diagonal elements may all be positive.

There are several examples of this behaviour which can be found in CALPHAD databases. For example, using the TCNI8 and MOBNI4 from Thermo-Calc for the alloy Ni-8 at.% Al-9 at.% W at 900°C one finds that the coefficient $D'_{WW}^{\text{Ni}} < 0$. If one rather chooses W as dependent species all diagonal coefficients are positive.

ideal behaviour except for quite diluted solutions or diffusion of isotopes in a pure element. Isotopes have the same chemical behaviour but may have different mobility. Anyhow, for an ideal solution the matrix $d\mu/dX$ is diagonal with diagonal elements RT/x_i . The diffusion coefficient matrix in the lattice-fixed frame of reference will then only contain the diagonal elements $RTV_m L_{ii}/x_i$. This matrix is thus positive definite and all diagonal elements are positive.

Transformation to number-fixed frame of reference and taking element N as dependent, yields diagonal coefficients of the type $RTV_m[(1-x_i)L_{ii}/x_i + x_iL_{NN}/x_N] > 0$, i.e. all diagonal elements must be positive. The same result will hold for a sufficiently dilute solution. In the number-fixed frame of reference off-diagonal elements of the type $x_iRTV_m[L_{NN}/x_N - L_{kk}/x_k]$ are introduced. They can be positive or negative depending on the conditions. In this case we cannot say if the D' matrix is positive definite but from section 5 it is clear that it must have positive eigenvalues and that its trace must be positive.

In a later work Castleman^[7] also discussed the signs of the diagonal elements in an ideal solution. Taking into account the vacancy wind effect analyzed by Manning^[8, 9] he found that mathematically it is possible to have negative diagonal coefficients even in a thermodynamically ideal

system provided that the differences in mobility are sufficiently large, typically 3 orders of magnitude. The vacancy-wind effect yields symmetric off-diagonal elements in the L matrix even in the lattice-fixed frame of reference. Although he concluded that it was possible he regarded the required conditions as physically unrealistic and concluded that the diagonal elements should be positive in an ideal system.

8 Conclusion

The fact that an individual diagonal diffusion coefficient is negative in the number-fixed frame of reference has no physical implications. By choosing another species as dependent species all diagonal elements may be turned positive. The only requirement is that the trace, i.e. the sum $\sum_{i=1}^{N-1} D_{ii}^N > 0$.

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