

THERMODYNAMICS OF DIFFUSION IN MULTICOMPONENT SYSTEMS

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Synopsis

The phenomenological description of diffusion in isotropic mixtures is developed from the expression for the entropy production and the relations between the diffusion coefficients, resulting from the Onsager relations, are derived. The results are specified for ternary mixtures.

§ 1. *Introduction.* In a previous paper ¹⁾, to be referred to hereafter as I, we have introduced the phenomenological description of the diffusion phenomenon and have given an appropriate definition of the diffusion coefficient for a binary mixture (*cf.* § I.7A). It is the purpose of the present paper to extend this description to the case of a multicomponent system and to derive the relations between the diffusion coefficients resulting from the Onsager relations (*cf.* also ²⁾).

As was already done in the case of a binary mixture, the diffusion of the components can be described with respect to various reference velocities, giving rise to different matrices of diffusion coefficients. The relations between these matrices follow from the transformations between the sets of diffusion flows, to which these matrices correspond (for ternary mixtures similar calculations have been given by Prigogine ³⁾).

The transformation formulae relating the various types of diffusion flows are derived in § 2. The corresponding transformation of the conjugated thermodynamic forces follows with the help of the treatment, developed previously ⁴⁾.

Starting from the expression for the entropy production, we can describe the diffusion most easily with respect to one of the components (*e.g.*, the solvent). This is done in § 3, where the corresponding phenomenological equations (Fick's law in the first form) and the diffusion matrix D are formulated and where the relations between the diffusion coefficients resulting from the Onsager relations are given. In § 4 the description with respect to an arbitrary mean velocity is derived from § 3 with the help of the transformation formulae of § 2. The connection with the coefficient of binary diffusion, introduced in § I.7A, is discussed in § 5. The differential equations for the diffusion (Fick's law in the second form) are deduced in § 6 and in § 7 the results are specified for a ternary mixture.

Since the phenomenological equations relate the diffusion flows to the gradients of the chemical potentials, one has to introduce the derivatives of the chemical potentials with respect to the concentrations in order to find Fick's law in the usual form. For these derivatives the Gibbs-Duhem relations hold and, in addition, a number of relations which (like Maxwell's relations) follow by cross differentiation of thermodynamic functions. They are derived in Appendix I. In Appendix II we give the derivatives of concentrations with respect to fractions and conversely for a ternary mixture.

§ 2. *Transformation formulae for the diffusion flows.* For a mixture of n components (labelled $k = 1, \dots, n$) with velocities \mathbf{v}_k we can introduce an arbitrary mean velocity

$$\mathbf{v}^a \equiv \sum_{k=1}^n w_k \mathbf{v}_k, \quad (\sum_{k=1}^n w_k = 1), \quad (1)$$

and define the diffusion flows \mathbf{J}_k^a with respect to \mathbf{v}^a

$$\mathbf{J}_k^a \equiv \varrho_k (\mathbf{v}_k - \mathbf{v}^a), \quad (k = 1, \dots, n), \quad (2)$$

which, according to the definition (1) of \mathbf{v}^a , satisfy the identity

$$\sum_{k=1}^n w_k \mathbf{J}_k^a / c_k = 0, \quad (3)$$

(c_k is the mass fraction ϱ_k/ϱ of component k). Examples of \mathbf{v}^a have been given in I, § 5A.

Let \mathbf{v}^b be an other mean velocity

$$\mathbf{v}^b \equiv \sum_{k=1}^n u_k \mathbf{v}_k, \quad (\sum_{k=1}^n u_k = 1), \quad (4)$$

and

$$\mathbf{J}_k^b \equiv \varrho_k (\mathbf{v}_k - \mathbf{v}^b), \quad (k = 1, \dots, n) \quad (5)$$

the corresponding flows satisfying the identity

$$\sum_{k=1}^n u_k \mathbf{J}_k^b / c_k = 0. \quad (6)$$

If $w_n \neq 0$ and $u_n \neq 0$ the $n - 1$ independent flows $\mathbf{J}_1^a, \dots, \mathbf{J}_{n-1}^a$ can be expressed in the independent flows $\mathbf{J}_1^b, \dots, \mathbf{J}_{n-1}^b$ by a linear transformation

$$\mathbf{J}_k^a = \sum_{i=1}^{n-1} P_{ki} \mathbf{J}_i^b, \quad (k = 1, \dots, n - 1), \quad (7)$$

where the matrix P is given by

$$P_{ki} = \delta_{ki} + (w_n u_i / u_n - w_i) c_k / c_i, \quad (i, k = 1, \dots, n - 1), \quad (8)$$

as follows in a straightforward manner by expressing both sides of (7) in terms of the independent velocities $\mathbf{v}_1, \dots, \mathbf{v}_n$, subsequently equating the coefficients of these velocities appearing on both sides of the equation. The inverse matrix P^{-1} follows from (8) by interchanging the weight factors u and w

$$P_{ki}^{-1} = \delta_{ki} + (u_n w_i / w_n - u_i) c_k / c_i, \quad (i, k = 1, \dots, n - 1). \quad (9)$$

The flows \mathbf{J}_n^a or \mathbf{J}_n^b are determined by the remaining $n - 1$ independent flows through (3) or (6).

If the contribution of the flows \mathbf{J}_k^a to the entropy production (per unit time and volume) is

$$\sigma_1 = \sum_{k=1}^{n-1} \mathbf{J}_k^a \cdot \mathbf{X}_k^a, \tag{10}$$

one can apply the linear transformation P^{-1} to the flows \mathbf{J}_k^a and rewrite the entropy production in the form

$$\sigma_1 = \sum_{k=1}^{n-1} \mathbf{J}_k^b \cdot \mathbf{X}_k. \tag{11}$$

As phenomenological equations one introduces linear relationships between the flows \mathbf{J}_k^a and the corresponding thermodynamic forces \mathbf{X}_k^a and similarly between the flows \mathbf{J}_k^b and the forces \mathbf{X}_k^b . From the treatment in ⁴) it follows that the validity of the Onsager reciprocity relations between the phenomenological coefficients is not affected by the transformation if the transformation matrix of the forces \mathbf{X}_k^a equals \tilde{P} (the symbol \sim indicates the transposed matrix), *i.e.*,

$$\mathbf{X}_k^b = \sum_{i=1}^{n-1} P_{ik} \mathbf{X}_i^a, \quad (k = 1, \dots, n - 1). \tag{12}$$

Finally, we may remark that the above transformation can also be performed in the absence of mechanical equilibrium.

§ 3. *Description of diffusion with respect to one of the components.* In order to describe diffusion phenomena in a multicomponent system we consider for the sake of brevity the simple case of an isotropic mixture of n non-reacting components which are not subject to external forces. Temperature gradients and viscous forces will not be taken into consideration. From the equation of motion (I. 10) it follows that the pressure will be uniform as soon as the system is at mechanical equilibrium ($d\mathbf{v}/dt = 0$, where \mathbf{v} is the centre of mass velocity as defined by (I. 3)).

We first write down the expression for the entropy production σ for this case which follows from the more general expression, given in § I. 3. With the assumption of mechanical equilibrium we can replace the centre of mass velocity in the diffusion flows occurring in the expression for σ by an arbitrary other reference velocity as was done in § I. 5A. Thus, for the present case we can take as a starting point equation (I.31) which reduces to

$$T\sigma = - \sum_{k=1}^n \mathbf{J}_k^a \cdot (\text{grad } \mu_k)_{P,T}, \tag{13}$$

with μ_k the chemical potential of component k .

If we take the velocity \mathbf{v}_n of the n th component (*e.g.*, the solvent in a solution) for the reference velocity \mathbf{v}^a and denote

$$\mathbf{J}_k^r \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}_n), \tag{14}$$

we are left with $n - 1$ independent flows in (13). Choosing P, T and the

concentrations $\varrho_1, \dots, \varrho_{n-1}$ as the state variables we can rewrite (13) as

$$T\sigma = - \sum_{k=1}^{n-1} \mathbf{J}_k^r \cdot \sum_{i=1}^{n-1} \mu_{ki} \text{grad } \varrho_i, \quad (15)$$

where

$$\mu_{ki} \equiv (\partial \mu_k / \partial \varrho_i)_{P, T, \varrho_j}, \quad (i, j = 1, \dots, n-1). \quad (16)$$

In view of (15) we introduce as phenomenological equations

$$\mathbf{J}_k^r = - \sum_{j=1}^{n-1} L_{kj} \sum_{i=1}^{n-1} \mu_{ji} \text{grad } \varrho_i = - \sum_{i=1}^{n-1} D_{ki} \text{grad } \varrho_i, \quad (k=1, \dots, n-1), \quad (17)$$

which defines the coefficients of diffusion with respect to one of the components

$$D_{ki} \equiv \sum_{j=1}^{n-1} L_{kj} \mu_{ji}, \quad (D = L\mu), \quad (18)$$

(between parentheses we have indicated the relation between the diffusion coefficients and the L_{kj} in matrix notation).

The Onsager reciprocal relations read

$$L_{kj} = L_{jk}, \quad (\tilde{L} = L), \quad (19)$$

or in terms of the diffusion coefficients

$$\sum_{j=1}^{n-1} D_{jk} \mu_{ji} = \sum_{j=1}^{n-1} \mu_{jk} D_{ji}, \quad (\tilde{D}\mu = \tilde{\mu}D), \quad (20)$$

which reduces the number of independent diffusion coefficients from $(n-1)^2$ to $\frac{1}{2}n(n-1)$.

§ 4. *Diffusion with respect to an arbitrary mean velocity.* In the foregoing section the diffusion has been described with respect to one of the components of the mixture. We now want to pass on to a description with respect to an arbitrary mean velocity. In order to do this we can take the phenomenological equations (17) as a starting point and transform from the flows \mathbf{J}_k^r to the flows \mathbf{J}_k^a defined by (2). With

$$\mathbf{J}_k^a = \sum_{i=1}^{n-1} P_{ki} \mathbf{J}_i^r, \quad (21)$$

where in view of (8) the matrix P is

$$P_{ki} = \delta_{ki} - w_i c_k / c_i, \quad (22)$$

it follows from (17) that

$$\mathbf{J}_k^a = - \sum_{j=1}^{n-1} P_{kj} \sum_{i=1}^{n-1} D_{ji} \text{grad } \varrho_i = - \sum_{i=1}^{n-1} D_{ki}^a \text{grad } \varrho_i, \quad (23)$$

which defines the diffusion coefficients D_{ki}^a . The diffusion matrix D^a is related to D by

$$D_{ki}^a = \sum_{j=1}^{n-1} P_{kj} D_{ji}, \quad (D^a = PD). \quad (24)$$

The Onsager relations now read

$$\sum_{j,l=1}^{n-1} D_{jk}^a P_{lj}^{-1} \mu_{li} = \sum_{j,l=1}^{n-1} \mu_{lk} P_{lj}^{-1} D_{ji}^a, \quad (\tilde{D}^a \tilde{P}^{-1} \mu = \tilde{\mu} P^{-1} D^a), \quad (25)$$

or with

$$v_{ji} \equiv \sum_{l=1}^{n-1} P_{lj}^{-1} \mu_{li}, \quad (v \equiv \tilde{P}^{-1} \mu), \quad (26)$$

also

$$\sum_{j=1}^{n-1} D_{jk}^a v_{ji} = \sum_{j=1}^{n-1} v_{jk} D_{ji}^a, \quad (\tilde{D}^a v = \tilde{v} D^a). \quad (27)$$

In deriving (23) we have taken the phenomenological equation (17) as a starting point and we have applied a linear transformation of the flows. Of course, the results of this section can also be achieved by a simultaneous transformation of fluxes *and* forces according to equations (7) and (12), subsequently introducing linear relationships between the transformed fluxes and forces. The phenomenological coefficients in these relations then will be connected to the coefficients L_{kj} of (17) in the same way as in equation (41) of reference 4). Again, we can introduce the diffusion matrix D^a and re-establish (24).

A third way to reach the above equations is to retain the general expression (13). However, since the n fluxes (and also the n forces) in (13) are interdependent, it is then necessary to eliminate one of the fluxes and one of the forces.

§ 5. *The connection with the binary diffusion coefficient D.* Of course, the foregoing descriptions also apply to binary mixtures. For that case we have defined in § I.7A a diffusion coefficient D which did not depend on the special choice of the weight factors w_k . In order to extend the description given in § I.7A to multicomponent systems, we introduce as the reference velocity the mean volume velocity

$$v^\circ \equiv \sum_{k=1}^n \varrho_k v_k \mathbf{v}_k, \quad (\sum_{k=1}^n \varrho_k v_k = 1), \quad (28)$$

and consider the phenomenological equations (23) for this special choice

$$\mathbf{J}_k^\circ \equiv \varrho_k (\mathbf{v}_k - \mathbf{v}^\circ) = - \sum_{i=1}^{n-1} D_{ki}^\circ \text{grad } \varrho_i. \quad (29)$$

On comparison of this equation with (I.68) we see that (29) reduces for $n = 2$ to (I.68) with $D = D_{11}^\circ$. The general definition (I.62) or (I.65) of D is also included in the present description and can be derived from (29). As a matter of fact, if we express the diffusion matrix D^a defined by (23) in terms of the D_{ki}° by

$$D_{ki}^a = \sum_{j=1}^{n-1} Q_{kj} D_{ji}^\circ, \quad (D^a = Q D^\circ), \quad (30)$$

where analogous to (8)

$$Q_{ki} = \delta_{ki} + (w_n \varrho_i v_i / \varrho_n v_n - w_i) c_k / c_i, \quad (31)$$

we can rewrite (23) in the form

$$\mathbf{J}_k^a = - \sum_{i=1}^{n-1} (Q D^\circ)_{ki} \text{grad } \varrho_i. \quad (32)$$

For $n = 2$ this reduces to

$$\mathbf{J}_1^a = - w_2 (\varrho_2 v_2)^{-1} D_{11}^\circ \text{grad } \varrho_1, \quad (33)$$

which is equation (I.65). So the matrix D° should be considered as the generalization of the binary diffusion coefficient D . The reciprocal relations for D° are included in (27).

In his paper on liquid diffusion Onsager⁵⁾ also considers diffusion flows with respect to \mathbf{v}° , but states that "it seems impossible to devise a simple general scheme of description for an n -component system which reduces directly to Fick's law with one single diffusion coefficient for the case $n = 2$ ". From the above it is clear how such a general scheme could be obtained. The reason why this reduction is not possible with Onsager's description is that in the latter treatment n^2 coefficients are introduced for $n > 2$, but only one single coefficient for $n = 2$. Thus n interdependent diffusion flows are chosen for $n > 2$ which are related to n interdependent concentration gradients. The situation thus met with is quite analogous to the one described in a paper with De Groot⁶⁾: there exists a number of relations between the phenomenological coefficients and, moreover, a certain arbitrariness in the definition of these coefficients. The transition to the case $n = 2$ with the use of independent quantities then cannot be performed directly but follows from the treatment given in reference⁶⁾, if one introduces in the phenomenological equations the appropriate thermodynamic forces, which are to be taken from the expression for the entropy production (these forces are the quantities $(\text{grad } \mu_k)_{P,T}$).

§ 6. *The differential equation for the diffusion.* In the absence of chemical reactions conservation of mass is expressed by

$$\partial \rho_k / \partial t = - \text{div } \rho_k \mathbf{v}_k = - \text{div } \mathbf{J}_k^a - \text{div } \rho_k \mathbf{v}^a. \quad (34)$$

For a closed vessel the boundary condition can always be expressed by the vanishing of some average of the absolute flows $\rho_k \mathbf{v}_k$ which means that for a certain choice of the weight factors w_k

$$\mathbf{v}^a \equiv \sum_{k=1}^n w_k \mathbf{v}_k = 0, \quad (35)$$

(e.g., if the partial specific volumes vary only slightly throughout the vessel, the mean volume velocity can be taken zero, cf. I, App. I). For this special choice of the reference velocity we can insert (23) in the conservation law (34):

$$\partial \rho_k / \partial t = \text{div } \sum_{i=1}^{n-1} D_{ki}^a \text{grad } \rho_i = \sum_{i=1}^{n-1} \{D_{ki}^a \Delta \rho_i + \text{grad } D_{ki}^a \cdot \text{grad } \rho_i\}. \quad (36)$$

If, moreover, these special diffusion coefficients D_{ki}^a would depend only slightly on the densities ρ_i , the last term of (36) could be neglected and the differential equation would take the simple form

$$\partial \rho_k / \partial t = \sum_{i=1}^{n-1} D_{ki}^a \Delta \rho_i. \quad (37)$$

§ 7. *Ternary mixtures.* For the case of a ternary mixture we have 4 diffusion coefficients between which one Onsager relation exists. For dif-

fusion with respect to a 'solvent' this relation reads

$$D_{11}\mu_{12} - D_{12}\mu_{11} = D_{22}\mu_{21} - D_{21}\mu_{22} \quad (38)$$

and for diffusion with respect to an arbitrary mean velocity analogously

$$D_{11}^a\nu_{12} - D_{12}^a\nu_{11} = D_{22}^a\nu_{21} - D_{21}^a\nu_{22}. \quad (39)$$

For this case the differential equations are

$$\partial\rho_k/\partial t = D_{k1}^a(\partial^2\rho_1/\partial x^2) + D_{k2}^a(\partial^2\rho_2/\partial x^2), \quad (k = 1, 2), \quad (40)$$

if the diffusion is a one-dimensional phenomenon.

APPENDIX I

In the derivation of (13) (*viz.*, in the proof of Prigogine's theorem which leads to (13)) use is made of the Gibbs-Duhem relation, which may be written

$$\sum_{j=1}^n \rho_j \mu_{jk} = 0, \quad (k = 1, \dots, n-1). \quad (41)$$

It should be noted that apart from these equations a number of additional relations exists between the derivatives μ_{kj} (and analogously between the ν_{kj}). Similar relations (*e.g.*, for the derivatives of chemical potentials or activities with respect to molalities, mole fractions or mole numbers) can be found in the literature ^{7) 8) 9)}.

In order to derive the relations which do apply in the present treatment, we choose P , T and the mass fractions c_1, \dots, c_{n-1} as state variables and start from the thermodynamic equation

$$dg = -s dT + v dP + \sum_{i=1}^n \mu_i dc_i = -s dT + v dP + \sum_{i=1}^{n-1} (\mu_i - \mu_n) dc_i \quad (42)$$

where g , s and v are the mean specific Gibbs function, entropy and volume, resp. By cross differentiation we find

$$\{\partial(\mu_k - \mu_n)/\partial c_i\}_{P,T,c_j} = \{\partial(\mu_i - \mu_n)/\partial c_k\}_{P,T,c_j}, \quad (43)$$

$$\text{or } \partial\mu_k/\partial c_i - \partial\mu_i/\partial c_k = \partial\mu_n/\partial c_i - \partial\mu_n/\partial c_k, \quad (i, k = 1, \dots, n-1). \quad (44)$$

With the help of the Gibbs-Duhem relation in the form

$$\sum_{j=1}^n c_j (\partial\mu_j/\partial c_k)_{P,T,c_l} = 0, \quad (k = 1, \dots, n-1), \quad (45)$$

we can eliminate μ_n from (44):

$$\partial\mu_k/\partial c_i - \partial\mu_i/\partial c_k = c_n^{-1} \sum_{j=1}^{n-1} c_j (\partial\mu_j/\partial c_k - \partial\mu_j/\partial c_i). \quad (46)$$

(An alternative starting point for the derivation of (44) is provided by the Euler relation

$$g = \sum_{l=1}^n c_l \mu_l, \quad (47)$$

from which one can easily derive (44) making use of

$$\partial^2 g / \partial c_i \partial c_k = \partial^2 g / \partial c_k \partial c_i \quad (48)$$

and of the Gibbs-Duhem relation).

For $i \neq k$ we have $\frac{1}{2}(n-1)(n-2)$ non-trivial relations (44) which are independent of the $n-1$ Gibbs-Duhem relations (45). Thus, the number of independent derivatives $\partial\mu_i/\partial c_i$ (with $l = 1, \dots, n; i = 1, \dots, n-1$) is diminished from $n(n-1)$ to $\frac{1}{2}n(n-1)$.

We now can pass on to the use of the densities ρ_i , instead of the fractions c_i . With (16) we have

$$(\partial\mu_k/\partial c_i)_{P,T,c_i} = \sum_{j=1}^{n-1} \mu_{kj} (\partial\rho_j/\partial c_i)_{P,T,c_i}. \quad (49)$$

For a ternary mixture the derivatives $\partial\rho_j/\partial c_i$ are given in App. II (59). For this case there is only one relation (46) which by means of (49) and (59) can be written as

$$\rho_1 v_2 \mu_{11} - (1 - \rho_2 v_2) \mu_{12} = \rho_2 v_1 \mu_{22} - (1 - \rho_1 v_1) \mu_{21}. \quad (50)$$

This relation gives rise to a corresponding one between the quantities ν_{kj} occurring in the description of diffusion with respect to an arbitrary mean velocity (cf. (26)):

$$\begin{aligned} \rho_1 \nu_{11} \{v_2(w_1 - 1) + w_2(1 - \rho_1 v_1)/\rho_2\} + \nu_{12} \{(1 - \rho_2 v_2)(1 - w_1) - w_2 \rho_1 v_1\} = \\ = \rho_2 \nu_{22} \{v_1(w_2 - 1) + w_1(1 - \rho_2 v_2)/\rho_1\} + \nu_{21} \{(1 - \rho_1 v_1)(1 - w_2) - w_1 \rho_2 v_2\}. \end{aligned} \quad (51)$$

This relation takes a very simple form for $w_k = \rho_k v_k$ (which means that the mean volume velocity is taken as the reference velocity of diffusion), *viz.*,

$$\nu_{12} = \nu_{21}. \quad (52)$$

Hence for this case the Onsager relation reads

$$D_{12}^\circ \nu_{11} - D_{21}^\circ \nu_{22} = \nu_{12} (D_{11}^\circ - D_{22}^\circ). \quad (53)$$

APPENDIX II

The phenomenological laws (17) and (23) connect the diffusion flows with the gradients of the *densities* of the components. Of course, we could as well have introduced the *fractions* of the various components as state variables. Then the diffusion coefficients would have referred to the gradients of these fractions. The advantage of this choice would manifest itself in the corresponding derivatives of the chemical potentials. For several cases (ideal solutions, regular solutions) these derivatives take a very simple form if they are taken with respect to the mole fractions (though the foregoing treatment has been set up for mass quantities it is obvious that we could have used molar quantities as well.) However, the law of conservation of mass takes its most simple form if densities are used and the same holds for the diffusion equations in the differential form.

In order to express the μ_{ki} in terms of the derivatives $\partial\mu_k/\partial c_i$ (for derivatives with respect to molar quantities the calculation goes along the same

lines) in the case of a ternary mixture we start with (49) where we still have to find the $\partial \rho_j / \partial c_i$. From

$$\sum_{k=1}^3 v_k (\delta \rho_k)_{P,T} = 0 \quad (54)$$

(cf. (I. 94)) and

$$(\delta \rho_k)_{P,T} = (\partial \rho_k / \partial c_1)_{P,T,c_2} \delta c_1 + (\partial \rho_k / \partial c_2)_{P,T,c_1} \delta c_2 \quad (55)$$

it follows that

$$\sum_{i=1}^2 \left\{ \sum_{k=1}^3 v_k (\partial \rho_k / \partial c_i) \right\} \delta c_i = 0, \quad (56)$$

or, since the δc_i are independent,

$$\sum_{k=1}^3 v_k (\partial \rho_k / \partial c_i) = 0, \quad (i = 1, 2). \quad (57)$$

Writing $\rho_1 = c_1 \rho$, $\rho_2 = c_2 \rho$, $\rho_3 = (1 - c_1 - c_2) \rho$ we then find

$$\partial \rho / \partial c_i = \rho^2 (v_3 - v_i), \quad (58)$$

and finally

$$\partial \rho_j / \partial c_i = \rho \delta_{ij} + \rho \rho_j (v_3 - v_i), \quad (i, j = 1, 2). \quad (59)$$

The Jacobian determinant of these four derivatives equals $\rho^3 v_3$. By inversion we find

$$\left. \begin{aligned} \partial c_1 / \partial \rho_1 &= \{1 + \rho_2 (v_3 - v_2)\} / \rho^2 v_3, \\ \partial c_1 / \partial \rho_2 &= -\rho_1 (v_3 - v_2) / \rho^2 v_3. \end{aligned} \right\} \quad (60)$$

The other derivatives are found by interchanging the subscripts 1 and 2.

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