

The Force and Friction Conception in the Diffusion of Multicomponent Systems

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The reciprocal relations of irreversible thermodynamics have been examined from the standpoint of the force and friction theory of pure diffusion. In cases where this theory is practicable, it gives a complete description in the sense that the reciprocal relations are dispensable. These latter are shown to be valid for relative flows, whereas the introduction of a special reference frame for the flows gives equations for which the reciprocal relations are not valid. — The force and friction theory contains throughout magnitudes of a direct physical significance, *e.g.* frictional coefficients of a uniform character. The latter coefficients are compared with those occurring in Onsagers theory of diffusion.

According to the force and friction conception, the dynamics¹ of pure diffusion in multicomponent systems is described by^{2,3}

$$-c_i \frac{\partial \mu_i}{\partial x} = \sum_{j=1}^k (C_j - C_i) \varphi_{ij} \quad (i = 1 \dots k) \quad (1)$$

These equations equalize, for each component i , the forces per unit volume; on the left hand side we have the driving force and on the right hand side the frictional forces for component i . The equations are written here for one-dimensional diffusion (in the x direction); c is the concentration in mole/cm³, μ the chemical potential, C the component velocity (the flow J_i divided by c_i), φ the friction/cm³ and k the number of components. The equations refer to the conditions in a volume element (dx).

In Onsagers system of description, the flows are written³

$$J_i = - \sum_{j=1}^k D_{ij} \frac{\partial c_j}{\partial x} \quad (2)$$

In addition to this we have² (*cf.* Refs.^{4,5})

$$J_i = - \sum_{j=1}^k \Omega_{ij} \frac{\partial \mu_j}{\partial x} \quad (3)$$

According to eqn. (1), the coefficients of eqn. (2) may be expressed in terms of frictions, thermodynamic factors, and concentrations. This will be treated in detail elsewhere⁷. We are, for the present, more interested in eqn. (3), in order to study the reciprocal relations $\Omega_{ij} = \Omega_{ji}$. The coefficients Ω may, according to eqn. (1) be expressed in terms of concentrations and frictions. For this purpose we must, however, have an additional condition for the flows, since otherwise the coefficients Ω are indeterminate. We may define the flows relative to a certain component (= the solvent as "macro-component" in Refs. 4,5), say component l , by the condition $J_l = 0$. It is, then, an easy matrix calculation to show that, if (as is physically self-evident) $\varphi_{ij} = \varphi_{ji}$, we must also have $\Omega_{ij} = \Omega_{ji}$ and *vice versa*. In view of this, it is difficult to see that the reciprocal relations of pure diffusion are, on principle, capable of giving any new information regarding the process.

The process is completely described in terms of concentrations, frictions and thermodynamic factors, and it can be stated *a priori* that the reciprocal relations can only, at most, yield relations between these magnitudes which are already known.

If, instead of reckoning the flows relative to a component l (see above), we prefer to define a reference frame for the flows³ by means of the equation $\sum J \bar{v}_i = 0$ (\bar{v} = partial molar volume), which has proved very useful in other connections, the coefficients no longer fulfil the condition $\Omega_{ij} = \Omega_{ji}$. Thus it seems that the conditions for a proper choice of fluxes and forces in Onsagers theory have to contain some restrictions regarding the reference frame for the fluxes, especially as the coefficients Ω are always indeterminate (0/0) if *no* additional condition for the flows is introduced.

It should be pointed out that if the force and friction conception is not used and the interpretation (as in the current treatment of the diffusion of gases) is directly concerned with the diffusion coefficients, the reciprocal relations are profitable in giving connections between these coefficients, see Ref.⁶.

In addition to eqn. (2), Onsagers system also contains the equations³.

$$\frac{\partial \mu_i}{\partial x} = - \sum_j R_{ij} J_j \quad (i = 1 \dots k) \quad (4)$$

If $c_j R_{ij}$ are denoted by Φ_{ij} , eqn. (4) may be written

$$\frac{\partial \mu_i}{\partial x} = - \sum_j \Phi_{ij} C_j \quad (5)$$

It is of interest to compare this with eqn. (1), now in the form

$$\frac{\partial \mu_i}{\partial x} = - \sum_j (C_i - C_j) \Phi_{i(j)} \quad (6)$$

where $\Phi_{i(j)}$ is the coefficient of *molar* friction of component i in relation to component j , *i. e.* the friction between the components i and j in a volume, containing one mole of i . It is seen that the two equations, (5) and (6), are identical if

$$\text{a) } \Phi_{ii} = \sum_{\substack{j \\ j \neq i}} \Phi_{i(j)} \quad \text{and b) } \Phi_{ij} = - \Phi_{i(j)} \quad (j \neq i) \quad (7)$$

Owing to $c_i c_j R_{ij} = -\varphi_{ij}$ ($j \neq i$), the symmetry of φ_{ij} automatically also leads to symmetry of the R_{ij} coefficients. Whereas the $\Phi_{i(i)}$ evidently do not exist, $\Phi_{ii} = 0$ or $R_{ii} = 0$ are physically unallowable assumptions.

The final aim for the diffusion measurements is to determine the φ -values of eqn. (1) through a solution of the corresponding differential equations ⁷. — As the diffusion theory can be outlined in different ways, it is appropriate to make reference also to the well-known work of de Groot ⁸ for other sides of the problem.

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