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THERMODYNAMICS OF SEDIMENTATION IN PAUCIDISPERSE SYSTEMS

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Synopsis

The previously given treatment of sedimentation phenomena in monodisperse uncharged systems with the help of thermodynamics of irreversible processes is extended to paucidisperse systems. The sedimentation rates of the components are derived by neglecting transverse effects and by introducing the boundary condition of vanishing volume flow. The results are specified for ternary ideal mixtures and the sedimentation coefficients are expressed in terms of diffusion coefficients.

The obtained equations might account for two effects, established in experimental sedimentation study, *viz.*, an anomalous behaviour of slowly sedimenting material above the boundary layer of more rapidly sedimenting components and the occurrence of a backward flow in experiments with the "synthetic boundary cell", where slowly sedimenting materials are mixed with more rapidly sedimenting ones.

§ 1. *Introduction.* In a previous paper [1]) (to which we shall refer as I) we have derived the general expression for the entropy production in rotating mixtures and formulated the phenomenological equations for sedimentation in monodisperse uncharged systems. In the present paper we want to extend this treatment to paucidisperse systems with particular emphasis on a description of the sedimentation process in ternary mixtures. The coefficients of diffusion for multicomponent systems, introduced in a preceding paper [2]) (in the following referred to as II), will be used.

The general form of the Onsager relations for vectorial phenomena in rotating systems is given in § 2. With the help of the expression for the entropy production, we formulate in § 3 the phenomenological equations for the fluxes of matter in rotating isothermal mixtures of uncharged components. In particular, we consider the fluxes with respect to the mean volume velocity. The spatial distribution of the components in sedimentation equilibrium is given in § 4 and is specified for ideal solutions.

The equations for the sedimentation velocities in paucidisperse systems are considered in detail in § 5. They are derived from the phenomenological equations by neglecting transverse effects and by introducing the boundary condition for a closed vessel, which for liquids leads to the vanishing of the mean volume velocity, previously chosen as the reference velocity.

For ternary mixtures the equations describe the effect of a boundary layer of one of the sedimenting components on the sedimentation velocity of the other. As is discussed in § 5*A*, this effect might in part account for a boundary anomaly, encountered in experimental investigations. The change in sedimentation velocity, due to the presence of other sedimenting materials is explicitly calculated in § 5*B* for ideal solutions. From the final equations it is clear, that in the region where both components have a finite density, each of the components can be slowed down by the other. This effect might explain the occurrence of a 'backward flow', encountered in sedimentation experiments where slowly sedimenting materials are mixed with more rapidly sedimenting ones. This effect also might contribute to the above mentioned boundary anomaly.

In the Appendix we give the formulae for the derivatives of the densities with respect to the chemical potentials for ideal solutions, used in § 5*A*.

§ 2. *The Onsager relations for vectorial phenomena in a rotating system or in a magnetic field.* In this section we give the Onsager reciprocal relations for vectorial processes in an isotropic medium, which is subject to an over-all rotation or placed in a uniform external magnetic field; the angular velocity or the magnetic field will be denoted by the comprehensive symbol H.

The contribution σ_v of the vectorial processes to the entropy production σ (per unit time and volume) can be given by [3])

$$T\sigma_v = \sum_{k=1}^{\nu} \mathfrak{J}_k \cdot \mathfrak{X}_k, \tag{1}$$

with ν independent fluxes $\mathfrak{J}_k$ and ν independent thermodynamic forces $\mathfrak{X}_k$. We then introduce the phenomenological equations

$$\mathfrak{J}_k = \sum_{i=1}^{\nu} \mathsf{L}_{ki} \cdot \mathfrak{X}_i, \qquad (k = 1, \ldots, \nu). \tag{2}$$

Each tensor L_{ki} can be split into a symmetrical and an antisymmetrical tensor with respect to space coordinates

$$\mathsf{L}_{ki} = \mathsf{L}^s_{ki} + \mathsf{L}^a_{ki}. \tag{3}$$

If the z-axis is chosen in the direction of H it follows from the isotropy of the medium that the relations (2) are invariant for rotation about the z-axis, hence

$$\mathsf{L}_{ki} = \begin{bmatrix} L^{11}_{ki} & L^{12}_{ki} & 0 \\ -L^{12}_{ki} & L^{11}_{ki} & 0 \\ 0 & 0 & L^{33}_{ki} \end{bmatrix} \tag{4}$$

or

$$\mathsf{L}^s_{ki} = \begin{bmatrix} L^{11}_{ki} & 0 & 0 \\ 0 & L^{11}_{ki} & 0 \\ 0 & 0 & L^{33}_{ki} \end{bmatrix} \quad \text{and} \quad \mathsf{L}^a_{ki} = \begin{bmatrix} 0 & L^{12}_{ki} & 0 \\ -L^{12}_{ki} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{5}$$

The number of phenomenological coefficients is thus reduced from $9\nu^2$ to $3\nu^2$. Moreover, it follows from the isotropy that the relations (2) are invariant for a rotation about an axis, perpendicular to the z-axis, by an angle π. From this it follows, that L^s_{ki} is an even function of H and L^a_{ki} is an odd function of H.

The Onsager reciprocal relations read [4] [5]

$$\mathsf{L}_{ki}(\mathrm{H}) = \mathsf{L}^{\dagger}_{ik}(-\mathrm{H}), \tag{6}$$

(where $\dagger$ indicates transposing of the Cartesian components), which can be written as

$$\mathsf{L}_{ki}(\mathrm{H}) = \mathsf{L}_{ik}(\mathrm{H}), \tag{7}$$

since

$$\begin{aligned} \mathsf{L}^s_{ki}(\mathrm{H}) &= \mathsf{L}^s_{ik}(-\mathrm{H}) = \mathsf{L}^s_{ik}(\mathrm{H}), \\ \mathsf{L}^a_{ki}(\mathrm{H}) &= \mathsf{L}^{a\dagger}_{ik}(-\mathrm{H}) = -\mathsf{L}^{a\dagger}_{ik}(\mathrm{H}) = \mathsf{L}^a_{ik}(\mathrm{H}), \end{aligned} \tag{8}$$

where we have used the parities of $\mathsf{L}^s_{ik}(\mathrm{H})$ and $\mathsf{L}^{a\dagger}_{ik}(\mathrm{H})$. So by means of the Onsager relations the number of independent coefficients is further reduced to $\frac{3}{2}\nu(\nu+1)$.

§ 3. *The phenomenological equations for sedimentation in paucidisperse systems.* As in I we consider a system of n non-reacting components, rotating with an angular velocity $\boldsymbol{\omega}$. At mechanical equilibrium the entropy production is again given by (I.31), where the flows $\mathbf{J}^a_k$ are taken with respect to the mean velocity $\mathbf{v}^a$. For this reference velocity we choose the velocity of the nth component (the solvent), the flow $\mathbf{J}^r_n$ then being zero. If the components do not carry electrical charges and if the system is isothermal, equation (I.31) then reduces to

$$T\sigma = \textstyle\sum_{k=1}^{n-1} \mathbf{J}^r_k \cdot \{(1-\varrho v_k)(\omega^2\mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\operatorname{grad}\mu_k)_{P,T}\}, \tag{9}$$

which is an extension of (II.15), since (9) gives the entropy production for diffusion in the presence of an external field.

According to (2) we introduce as phenomenological equations

$$\mathbf{J}^r_k = \textstyle\sum_{i=1}^{n-1} \mathsf{L}_{ki} \cdot \{(1-\varrho v_i)(\omega^2\mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\operatorname{grad}\mu_i)_{P,T}\}, \quad (k=1, \ldots, n-1), \tag{10}$$

which is the extension of (II.17) to the present case. The tensors L_{ki} satisfy the Onsager relations (7) with $\mathrm{H} = \boldsymbol{\omega}$.

By a linear transformation of (10) (in the same way as was done in § 4 and 5 of II)we can find the phenomenological equations for the flows $\mathbf{J}^\circ_k$ with respect to the mean volume velocity

$$\mathbf{v}^\circ = \textstyle\sum_{k=1}^{n} \varrho_k v_k \mathbf{v}_k, \tag{11}$$

making use of the matrix P which transforms the flows $\mathbf{J}^r_k$ into the flows $\mathbf{J}^\circ_k$,

$$\mathbf{J}^\circ_k \equiv \varrho_k(\mathbf{v}_k - \mathbf{v}^\circ) = \textstyle\sum_{i=1}^{n-1} P_{ki}\, \mathbf{J}^r_i, \quad (k = 1, \ldots, n-1), \tag{12}$$

where, according to (II.22) for $w_i = \varrho_i v_i$,

$$P_{ki} = \delta_{ki} - \varrho_k v_i. \tag{13}$$

The phenomenological equations (10) then yield

$$\mathbf{J}_k^\circ = \sum_{i=1}^{n-1} \mathsf{L}'_{ki} \cdot \{(1 - \varrho v_i)\,(\omega^2 \mathbf{r} + 2\mathbf{v} \wedge \boldsymbol{\omega}) - (\operatorname{grad} \mu_i)_{P,T}\}, \tag{14}$$

where

$$\mathsf{L}'_{ki} = \sum_{j=1}^{n-1} P_{kj}\, \mathsf{L}_{ji}. \tag{15}$$

The phenomenological equations (14) are the basic equations for our description of sedimentation in paucidisperse systems.

N.B. We might remark that for the tensors L'_{ki} the Onsager relations do not hold in the form (7), since in passing on from (10) to (14) we have not performed a simultaneous transformation of the thermodynamic forces (*cf* [6])).

§ 4. *The sedimentation equilibrium.* Inasmuch as thermostatic equilibrium is characterized by the vanishing of the entropy production, it follows from (9) and (10) or (14) that the flows and the corresponding thermodynamic forces vanish. The vanishing of the fluxes means that $\mathbf{v}_1 = \ldots = \mathbf{v}_n = 0$ in a closed vessel. Thus, the centre of mass velocity $\mathbf{v}$ equals zero and we find for $k = 1, \ldots, n - 1$ the well-known equilibrium equation

$$(1 - \varrho v_k)\omega^2 \mathbf{r} - (\operatorname{grad} \mu_k)_{P,T} = 0, \tag{16}$$

which, as a consequence, also holds for $k = n$ (this follows immediately with the help of (I.50) and (I.51)).

These equations describe the distribution of the components in sedimentation equilibrium. Choosing P, T and the mole fractions $n_1, \ldots, n_{n-1}$ as state variables we can rewrite (16) as

$$\sum_{i=1}^{n-1} (\partial \mu_k / \partial n_i)_{P,T,n_j} \operatorname{grad} n_i = (1 - \varrho v_k)\omega^2 \mathbf{r}. \tag{17}$$

For ideal solutions, where

$$(\partial \mu_k / \partial n_i)_{P,T,n_j} = RT \delta_{ki} / M_k n_k, \tag{18}$$

we find for each of the n components

$$n_k^{-1} \operatorname{grad} n_k = M_k (1 - \varrho v_k)\omega^2 \mathbf{r} / RT, \tag{19}$$

analogous to (I.58).

In order to express the equilibrium distribution in terms of the mass fractions c_i we need the derivatives

$$\partial c_k / \partial n_i = c_i \{M_i \delta_{ki} - c_k (M_i - M_n)\} / M_i n_t, \quad (k, i = 1, \ldots, n - 1), \tag{20}$$

with the help of which we find

$$c_k^{-1} \operatorname{grad} c_k = \{M_k (1 - \varrho v_k) - \sum_{i=1}^{n} c_i M_i (1 - \varrho v_i)\}\, \omega^2 \mathbf{r} / RT, \tag{21}$$

which also holds for $k = n$ and includes (I.59) for binary mixtures.

§ 5. *The sedimentation velocity in paucidisperse systems.* The phenomenological equations (14) enable us to find expressions for the sedimentation velocity in paucidisperse systems.

If we neglect, as we also did in I, all transverse effects, the Coriolis force in (14) can be left out and the tensors L'_{ki} reduce for an isotropic solution to scalar coefficients L'_{ki}, hence

$$\mathbf{J}^{\circ}_k = \sum_{i=1}^{n-1} L'_{ki} \{(1 - \varrho v_i)\, \omega^2 \mathbf{r} - \sum_{j=1}^{n-1} \mu_{ij} \operatorname{grad} \varrho_j\}. \tag{22}$$

Here μ_{ij} stands for $(\partial\mu_i/\partial\varrho_j)_{P,T,\varrho_k}$. The coefficient of $-$ grad ϱ_j in this equation is the diffusion coefficient D°_{kj}, introduced in (II.29). So we can write

$$\sum_{i=1}^{n-1} L'_{ki}\, \mu_{ij} = D^{\circ}_{kj}, \qquad (L' = D^{\circ}\mu^{-1}). \tag{23}$$

The coefficients D°_{kj} satisfy the Onsager relations in the form (II.27).

In particular, we want to consider a ternary mixture, a case that is frequently met with in ultracentrifuge measurements. As was shown in I (App. I) the boundary condition for a closed vessel can be expressed by the vanishing of the mean volume velocity $\mathbf{v}^{\circ}$ with the assumption that the partial specific volumes v_k do not appreciably depend on pressure and concentrations. For a ternary mixture the sedimentation velocities are then given by

$$\varrho_k \mathbf{v}_k = \sum_{j=1}^{2} D^{\circ}_{kj} \{\sum_{i=1}^{2} \mu^{-1}_{ji} (1 - \varrho v_i)\, \omega^2 \mathbf{r} - \operatorname{grad} \varrho_j\}, \quad (k = 1, 2). \tag{24}$$

In these equations four diffusion coefficients occur, which are interrelated by the Onsager relation

$$\nu^{-1}_{11} D^{\circ}_{21} - \nu^{-1}_{22} D^{\circ}_{12} = \nu^{-1}_{12} (D^{\circ}_{11} - D^{\circ}_{22}), \quad (\widetilde{D^{\circ}\nu^{-1}} = D^{\circ}\nu^{-1}), \tag{25}$$

(cf. (II.27) or (II.53)), where the coefficients ν^{-1}_{ki} follow from the μ^{-1}_{kj} according to (II.26)

$$\nu^{-1}_{ki} = \sum_{j=1}^{2} \mu^{-1}_{kj} P_{ij}, \qquad (\nu^{-1} = \mu^{-1} \tilde{P}), \tag{26}$$

or, with (13),

$$\nu^{-1}_{ki} = \mu^{-1}_{ki} (1 - \varrho_i v_i) - \mu^{-1}_{kj} \varrho_i v_j, \quad (i, j, k = 1, 2;\, i \neq j). \tag{27}$$

The coefficients μ^{-1}_{ki} (the derivatives $(\partial\varrho_k/\partial\mu_i)_{PT,\mu_j}$) together form the matrix μ^{-1}, which is the inverse of the matrix μ of derivatives μ_{ki}. For an ideal solution μ^{-1} is given in the Appendix.

From (24) one could in principle derive the mutual influence of the components on the sedimentation velocities and, by solving the differential equation resulting from the insertion of (24) in the law of conservation of mass (analogous to § II.6), determine the distribution of the components in the course of the sedimentation process. This would require the knowledge of the derivatives μ^{-1}_{ki} and the diffusion coefficients, in particular the cross coefficients D°_{12} and D°_{21}. However, some simple conclusions can be drawn

already from (24), which might account for two effects, established in experimental sedimentation study. These will be described in the following sections.

A. The influence of boundary layers on sedimentation velocities. As was first discovered by Johnston and Ogston [7] [8], an anomalous behaviour in the sedimentation patterns of mixtures is caused by a boundary anomaly. There is an apparent increase (a 'build up') of the amount of the less rapidly sedimenting component with a corresponding decrease in the amount of the other in the region above the boundary of faster mobility. The magnitude of the effect always increases with increase in solute concentration.

One contribution to this effect seems to be described immediately by the equations (24). In fact, let the boundary layer of 2 be closer to the outer wall than the boundary of 1 (component 2 may be the more rapidly sedimenting one). In the boundary region of 2, grad ϱ_2 is positive and very large, whereas on both sides of this layer grad ϱ_2 is negligible. According to (24), grad ϱ_2 contributes to $\varrho_1\mathbf{v}_1$ by the term $-D^{\circ}_{12}$ grad ϱ_2. If now D°_{12} is positive, $\mathbf{v}_1$ will be *smaller* in the boundary region of 2 than on both sides of this boundary, even if D°_{12} is small. This situation will give rise to an increase of the amount of 1 over and above its original value in the region above the boundary of 2.

Since grad ϱ_2 increases for larger values of ϱ_2 (the width of the boundary layer in first approximation being independent of ϱ_2), the magnitude of this effect indeed increases with increase in solute concentration, as was indicated by the experimental analysis.

Another possible contribution to the 'build up' will be described below.

B. Slowing down and backward flow during ultracentrifugation. In the foregoing we considered the influence of a density *gradient* of one of the components on the sedimentation velocity of the other. The description of the influence of the *densities* ϱ_1 and ϱ_2 on the sedimentation rates would require the knowledge of the derivatives μ_{ji}^{-1} and the dependence of the diffusion coefficients D°_{kj} on the composition.

In the following we shall assume ideality of the solution. We then find (*cf.* Appendix)

$$\mu_{ji}^{-1} = \varrho_j \{M_j\delta_{ji} - \varrho_i(\bar{v}_i - \bar{v}_3)\}/RT, \tag{28}$$

hence (24) reads

$$\begin{aligned}\varrho_2\mathbf{v}_2 = {} & \varrho_2 D^{\circ}_{22}\,[(1-\varrho v_2)\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3)\} - \varrho_1(1-\varrho v_1)\,(\bar{v}_1 - \bar{v}_3)]\omega^2\mathbf{r}/RT \\ & + \varrho_1 D^{\circ}_{21}\,[(1-\varrho v_1)\{M_1 - \varrho_1(\bar{v}_1 - \bar{v}_3)\} - \varrho_2(1-\varrho v_2)\,(\bar{v}_2 - \bar{v}_3)]\omega^2\mathbf{r}/RT \\ & - D^{\circ}_{22}\,\mathrm{grad}\,\varrho_2 - D^{\circ}_{21}\,\mathrm{grad}\,\varrho_1.\end{aligned} \tag{29}$$

The analogous expression for $\mathbf{v}_1$ follows by interchanging the subscripts 1 and 2. $\bar{v}_i$ is the partial molar volume

$$\bar{v}_i = M_i v_i. \tag{30}$$

We suppose the velocity of the boundary layer 1 to be given by $\mathbf{v}_1$ (A) in the region A between the two layers (where $\varrho_2 = 0$) and, likewise, the velocity of layer 2 by $\mathbf{v}_2(B)$ in the region B between layer 2 and the outer wall. Within these regions grad ϱ_1 = grad $\varrho_2 = 0$.

As long as the region A exists, the sedimentation rate of component 1 is given by

$$\mathbf{v}_1(A) = (1 - \varrho v_1)D_{11}^{\circ}\{M_1 - \varrho_1(\bar{v}_1 - \bar{v}_3)\}\omega^2\mathbf{r}/RT, \tag{31}$$

which equals (I.78), as it should be, because in this period component 1 sediments as in the case of a monodisperse system. We can rewrite (31) as

$$\mathbf{v}_1(A) = (1 - \varrho v_1)D_{11}^{\circ} M_1\{1 - \varrho_1 v_1 (1 - \bar{v}_3/\bar{v}_1)\}\omega^2\mathbf{r}/RT. \tag{32}$$

Usually, the partial molar volume of component 1 is very large in comparison with the partial molar volume of the solvent ($\bar{v}_1 \gg \bar{v}_3$). We then have

$$\mathbf{v}_1(A) = (1 - \varrho v_1)D_{11}^{\circ} M_1(1 - \varrho_1 v_1)\omega^2\mathbf{r}/RT, \tag{33}$$

which for a dilute solution ($\varrho_1 v_1 \ll 1$) reduces to the Svedberg equation (I.80) with $D = D_{11}^{\circ}$.

Let us now consider the region B, where both components are present. $\mathbf{v}_2$ is given by (29) with grad ϱ_1 = grad $\varrho_2 = 0$.

If M_2 is not too small with respect to M_1 (we suppose $M_3 < M_2 < M_1$), the factors occurring after D_{22}° and D_{21}° in (29) are of the same order of magnitude in practical cases. Inasmuch as cross coefficients tend to zero for dilute solutions ($|D_{21}^{\circ}| \ll D_{22}^{\circ}$), $\mathbf{v}_2$ will then be determined by the first term on the right-hand side of (29), which can be written

$$\mathbf{v}_2(B) = (1 - \varrho v_2)D_{22}^{\circ}\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3) - \varrho_1(\bar{v}_1 - \bar{v}_3)\}\omega^2\mathbf{r}/RT, \tag{34}$$

since v_1 and v_2 are nearly the same. Similarly we then have

$$\mathbf{v}_1(B) = (1 - \varrho v_1)D_{11}^{\circ}\{M_1 - \varrho_1(\bar{v}_1 - \bar{v}_3) - \varrho_2(\bar{v}_2 - \bar{v}_3)\}\,\omega^2\mathbf{r}/RT. \tag{35}$$

These equations describe the decrease in velocity of each component, due to the presence of the other component and, in particular, the slowing down of component 2 in the region B and hence a decrease in the sedimentation rate of 2, due to the finite value of ϱ_1.

We also can express this result in terms of sedimentation coefficients. In the absence of component 1 we have, analogous to (31),

$$\mathbf{v}_2 \equiv s_2^0\omega^2\mathbf{r} = (1 - \varrho v_2)D_{22}^{\circ}\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3)\}\omega^2\mathbf{r}/RT. \tag{36}$$

which defines s_2^0, the sedimentation coefficient for component 2 in the absence of component 1. Here D_{22}° is a binary diffusion coefficient. We can rewrite (34) as

$$\mathbf{v}_2(B) \equiv s_2\omega^2\mathbf{r} = (1 - \varrho v_2)D_{22}^\circ\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3)\} \times \\ \times [1 - \varrho_1(\bar{v}_1 - \bar{v}_3)/\{M_2 - \varrho_2(\bar{v}_2 - \bar{v}_3)\}]\omega^2\mathbf{r}/RT, \qquad (37)$$

which defines the sedimentation coefficient s_2 of component 2 in the ternary mixture. For infinite dilution of component 1 the coefficient D_{22}° in (37) will tend to the value for binary diffusion, occurring in (36). Taking the same value of ϱ in (36) and (37), neglecting $\bar{v}_3$ with respect to $\bar{v}_2$ and $\bar{v}_1$ and assuming $\varrho_2 v_2 \ll 1$, we therefore have in good approximation

$$s_2 = s_2^0(1 - \varrho_1 v_1 M_1/M_2). \qquad (38)$$

If $M_2 \ll M_1$, the second term of (29) in general cannot be neglected in the region B. Since this term will have the sign of D_{21}°, its contribution to $\mathbf{v}_2(B)$ will depend on the sign of D_{21}° and on the magnitude of $|D_{21}^\circ|$ as compared with D_{22}°. If D_{21}° is negative, the term under consideration gives an extra contribution to the slowing down of component 2, caused by the presence of the other component. In order to estimate the change in $\mathbf{v}_2$ if D_{21}° is positive, we can take together all the terms in (29) containing ϱ_1. If we assume $\bar{v}_3 \ll \bar{v}_2$ (as is the case in sedimentation experiments) we have as a consequence $\bar{v}_3 \ll \bar{v}_1$ and the result of the presence of component 1 then can be seen to depend essentially on the sign of

$$-\varrho_2 v_1 D_{22}^\circ + (1 - \varrho_1 v_1)D_{21}^\circ. \qquad (39)$$

Thus, also in this case component 2 will be slowed down if $D_{21}^\circ/D_{22}^\circ$ is smaller than $\varrho_2 v_1/(1 - \varrho_1 v_1)$.

According to the foregoing discussion, the equation (29) might account for the backward flow of slowly sedimenting materials in the presence of more rapidly sedimenting components, which occurs in experiments with the 'synthetic boundary cell' [9]): if 1 is more rapidly sedimenting than 2, the boundary of 1 overtakes the boundary of 2, merges with it and finally appears on the other side. The experiments showed that during the first part of the run there may be a backward flow of component 2. This effect might be explained by the foregoing description if the contribution of the term with D_{21}° is either negligible or negative.

The above treatment also suggests another contribution to the effect, mentioned in the preceding section A: the 'build up' of component 1 in the region A. From the discussion of equation (29) it is clear that, if $M_1 \lessapprox M_2$ (as was the case in actual experiments), component 1 will be slowed down in the region B as a result of the presence of component 2, the decrease in $\mathbf{v}_1$ being proportional to ϱ_2 (*cf.* (35)). This in turn might contribute to

a build up of component 1 in the region A, the effect increasing for larger values of ϱ_2.

APPENDIX

In order to calculate the derivatives μ_{ji}^{-1} for ideal ternary mixtures we first take P, T and the mole fractions n_1, n_2 as state variables. We then have

$$\partial\mu_k/\partial n_i = RT\delta_{ki}/M_k n_k, \tag{40}$$

and inversely

$$\partial n_k/\partial\mu_i = M_k n_k \delta_{ki}/RT. \tag{41}$$

The derivatives μ_{ji}^{-1} follow from

$$\mu_{ji}^{-1} \equiv \partial\varrho_j/\partial\mu_i = \textstyle\sum_{k=1}^{2} (\partial\varrho_j/\partial n_k)\,(\partial n_k/\partial\mu_i), \tag{42}$$

where we still have to find the $\partial\varrho_j/\partial n_k$. Since

$$\varrho_j = M_j n_j N, \tag{43}$$

(N is the total molar density) and, analogous to (II.58),

$$\partial N/\partial n_k = N^2(\bar{v}_3 - \bar{v}_k), \tag{44}$$

where $\bar{v}_k$ is the partial molar volume of component k, we find

$$\partial\varrho_j/\partial n_k = \varrho_j\,\{n_j^{-1}\delta_{jk} - N(\bar{v}_k - \bar{v}_3)\}. \tag{45}$$

The insertion of (41) and (45) into (42) yields (28).

The coefficients ν_{ki}^{-1}, occurring in the Onsager relation (25), are given by (27). For an ideal solution they follow by combining (27) and (28).

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