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DIFFUSION FORCES AND PHENOMENOLOGICAL COEFFICIENTS FOR A GAS MIXTURE

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ABSTRACT: The different selections of fluxes and the corresponding thermodynamic forces in the linear theory of irreversible thermodynamics are written. In this paper we present a method for calculating explicitly these forces by means of the equation of state of our gas mixture. Also, we will obtain the phenomenological coefficients of the linear laws in the standard form, as a function of some coefficients easily obtainable by experimental methods, using again the equation of state of the gas mixture. This last point will be treated for a binary mixture only.

INTRODUCTION

Irreversible thermodynamics is a branch of physical chemistry which extends the phenomenological treatment of thermodynamics to non-equilibrium processes.

Thermodynamics of irreversible processes takes into account many phenomenae, as mass transport, momentum and energy. It uses the hydrodynamic equations on a fundamental form, and its principal objectives are the viscosity effects, heat conduction, diffusive phenomenae and also cross effects as thermodiffusion.

In the same way as equilibrium thermodynamics, thermodynamics of irreversible processes is built upon two laws. The first law that defines internal energy and postulates energy conservation, can be written in the following form[1]

$$dU/dt = -V\,\mathrm{div}\,\mathbf{J}_q - P(dV/dt) - V\Pi:\,\mathrm{grad}\,\mathbf{v} + V\sum_{k=1}^{n}\mathbf{J}_k\cdot\mathbf{F}_k\ , \tag{1}$$

where U is the specific internal energy, V the specific volume, P the pressure, $\mathbf{J}_q$ the heat flux, $\mathbf{v}$ the hydrodynamic velocity of the mixture's center of mass, $J = \rho_k(\mathbf{v}_k - \mathbf{v})$ is the diffusion flux of the k component, $\mathbf{F}_k$ is the external force per unit mass exerted on the k component and Π is the viscosity tensor (pressure tensor without the hydrostatic part P).

The second law is built using the Gibbs relation on a mass element of our system. (That is, thermodynamical equilibrium is supposed to exist in each mass element which composes the system). In this way, the entropy production (which is zero for equilibrium processes) is obtained as[1]

$$\begin{aligned} T\sigma = {} & -\mathbf{J}_q\cdot(\mathrm{grad}\,T/T) - \sum_{k=1}^{n-1}\mathbf{J}_k\cdot\{T\,\mathrm{grad}\big((\mu_k/m_kT) - (\mu_n/m_nT)\big) - \mathbf{F}_k + \mathbf{F}_n\} - \\ & - \dot{\Pi}:(\dot{\mathrm{grad}}\ \mathbf{v})^{s} - \pi\,\mathrm{div}\,\mathbf{v} - \sum_{j=1}^{r} J_jA_j \end{aligned} \tag{2}$$

where σ is the entropy produced per unit time and unit volume, T is the temperature, μ_k the chemical potential per particle of the k component, m_k is the mass of a particle of this component, $\dot{\Pi} = \Pi - (\tfrac{1}{3}\Pi:\mathbf{U})\,\mathbf{U}$ where $\mathbf{U}$ is the three-dimensional unit matrix, $(\dot{\mathrm{grad}}\ \mathbf{v})^{s}$ is the symmetric part of the tensor $\dot{\mathrm{grad}}\ \mathbf{v} = \mathrm{grad}\ \mathbf{v} - (\tfrac{1}{3}\,\mathrm{div}\,\mathbf{v}')\,\mathbf{U}$, J_j is the chemical reaction rate of reaction j, $A_j = \sum_{k=1}^{n}\nu_{kj}(\mu_k/m_k)$ is the chemical affinity of chemical reaction j, where the quantity ν_{kj} divided by the molecular mass is the stoichiometric coefficient with which the k component appears in the chemical reaction j and finally $\pi = \frac{1}{3}\Pi : \boldsymbol{U}$. On deducing (2) we have used the fact that $\sum_{k=1}^{n} \boldsymbol{J}_k = 0$ and that Π is a symmetric tensor.

This last equation can be rewritten in the following matricial form

$$T\sigma = \tilde{\boldsymbol{X}}\,\boldsymbol{J} \tag{3}$$

where the tilde indicates the transposed vector and the vectors $\boldsymbol{X}$ and $\boldsymbol{J}$ are defined by

$$\tilde{\boldsymbol{J}} = (\boldsymbol{J}_q, \boldsymbol{J}_1, \ldots, \boldsymbol{J}_{n-1}, \dot{\Pi}_{11}, \dot{\Pi}_{12}, \dot{\Pi}_{13}, \dot{\Pi}_{21}, \dot{\Pi}_{22}, \dot{\Pi}_{23}, \dot{\Pi}_{31}, \dot{\Pi}_{32}, \dot{\Pi}_{33}, \pi, J_1, \ldots, J_r) \tag{4}$$

$$\begin{aligned}
\tilde{\boldsymbol{X}} = \Big(&-(\mathrm{grad}\, T/T),\ -\{T\ \mathrm{grad}\,[(\mu_1/m_1 T) - (\mu_n/m_n T)] - \boldsymbol{F}_1 + \boldsymbol{F}_n\}, \ldots, -\\
&-\{T\ \mathrm{grad}\,[(\mu_{n-1}/m_{n-1} T) - (\mu_n/m_n T)] - \boldsymbol{F}_{n-1} + \boldsymbol{F}_n\},\\
&-(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{11}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{12}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{13}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{21}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{22},\\
&-(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{23}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{31}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{32}, -(\dot{\mathrm{grad}}\ \mathbf{v})^{s}_{33}, -\mathrm{div}\ \mathbf{v}, -A_1, \ldots, -A_r\Big)
\end{aligned} \tag{5}$$

The $\boldsymbol{X}$ vector will be called the thermodynamic forces vector and the $\boldsymbol{J}$ vector will be the fluxes vector.

It is an experimental fact that the fluxes are linear functions of the thermodynamic forces when the system is not so far from equilibrium. That is

$$\boldsymbol{J} = \mathbf{L}\boldsymbol{X} \tag{6}$$

The $\mathbf{L}$ matrix is known as the phenomenological coefficients tensor and it is of such form that for an isotropic medium, it only relates the fluxes and forces of the same tensorial character. This fact is often referred to as the Curie symmetry principle.

The linear relations (6) for an isotropic medium can then, be written, for the fluxes and forces of vectorial character, in the following way

$$J_q = -L_{qq}(\text{grad }T/T) - \sum_{k=1}^{n-1} L_{qk}\left[T \text{ grad}\left((\mu_k/m_kT) - (\mu_n/m_nT)\right) - F_k + F_n\right] \tag{7}$$

$$J_i = -L_{iq}(\text{grad }T/T) - \sum_{k=1}^{n-1} L_{ik}\left[T \text{ grad}\left((\mu_k/m_kT) - (\mu_n/m_nT)\right) - F_k + F_n\right], \quad i = 1, \ldots, n-1 \tag{8}$$

It has been shown that the coefficients of the linear laws fulfill certain symmetry properties known as the Onsager reciprocal relations. For example $L_{qk} = L_{kq}$ in equations (7) and (8). In other words, the matrix which relates the fluxes and forces of vectorial character is a symmetrical matrix.

MEIXNER TRANSFORMATIONS

It is possible to put the entropy production (2) in equivalent forms with different selections of fluxes and forces. This is generally done for the entropy production due to fluxes and forces of vectorial character (the first two terms of the right hand in (2)), but it can be made for all terms in (2).[2] Such transformations are called Meixner transformations.

Let J and X be the vectors that consist of the first n components of (4) and (5); that is, the fluxes and forces of vectorial character only. Then

$$J = \mathbf{L}X \tag{9}$$

where $\mathbf{L}$ is a symmetric matrix. If we consider now a new set of fluxes and forces, linear functions of the previous two:

$$\begin{aligned} J' &= \mathbf{B}J \\ X' &= \mathbf{C}X \end{aligned} \tag{10}$$

where $\mathbf{C}$ is a non-singular matrix; then, it is seen that there exists a new relation between the new fluxes and forces in analogy to (9), with a new matrix of phenomenological coefficients:

$$\begin{aligned} J' &= \mathbf{L}' X' \\ \mathbf{L}' &= \mathbf{BLC}^{-1} \end{aligned} \qquad (11)$$

If we also ask that the Onsager reciprocal relations are still valid for the new matrix:

$$\tilde{\mathbf{L}}' = \mathbf{L}' \quad , \qquad (12)$$

and that the value of the entropy production remains the same:

$$T\sigma = \tilde{X}' J' \quad , \qquad (13)$$

where $\tilde{X}'$ and $\tilde{J}'$ are the vectors (4) and (5) with its first n components changed by the Meixner transformation (10). Then, it can be shown that

$$\mathbf{C} = \tilde{\mathbf{B}}^{-1} \quad . \qquad (14)$$

On using a matrix $\mathbf{B}$ defined by[2, 3]

$$\mathbf{B} \equiv \begin{pmatrix} I & -\left((H_1/m_1) - (H_n/m_n)\right) I & \dots & -\left((H_{n-1}/m_{n-1}) - (H_n/m_n)\right) I \\ 0 & I & \dots & 0 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ 0 & 0 & \dots & I \end{pmatrix}$$

$$(15)$$

where H_k is the partial enthalpy per particle:

$$H_k \equiv \left(\partial H / \partial N_k\right)_{T,P,\{N_j{}'s \neq k\}} \quad , \qquad (16)$$

and I is the three-dimensional unit matrix, the entropy production (2) can be written in the equivalent form

$$T\sigma = -\mathbf{J}_q' \cdot (\text{grad } T/T) - \sum_{k=1}^{n-1} \mathbf{J}_k \cdot [\{\text{grad}\,((\mu_k/m_k) - (\mu_n/m_n))\}_T - \mathbf{F}_k + \mathbf{F}_n] -$$

$$- \dot{\Pi} : (\text{gr}\dot{\text{a}}\text{d } \mathbf{v})^s - \pi \text{ div } \mathbf{v} - \sum_{j=1}^{r} J_j A_j \quad , \tag{17}$$

where

$$\mathbf{J}_q' \equiv \mathbf{J}_q - \sum_{k=1}^{n} (\mathbf{H}_k/m_k)\, \mathbf{J}_k \tag{18}$$

and

$$(\text{grad } \mu_k)_T \equiv \text{grad } \mu_k - (\partial\mu_k/\partial T)_{P,\{N's\}} \text{ grad } T \ . \tag{19}$$

On obtaining (17), we used the fact that

$$(\text{grad } \mu_k)_T = T \text{ grad } (\mu_k/T) + (\mathbf{H}_k/T) \text{ grad } T \tag{20}$$

which can be seen from the definition (19), from the equation

$$\mathbf{H}_k = T\mathbf{S}_k + \mu_k \tag{21}$$

where $\mathbf{S}_k$ is defined in the same way as definition (16), and also from the Maxwell relation:

$$\mathbf{S}_k = -(\partial\mu_k/\partial T)_{P,\{N_j's\}} \tag{22}$$

Another form of the entropy production can be obtained by means of the following matrix[2,3]

$$\mathbf{B} = \begin{pmatrix} (1/T)I & -\big((\mu_1/m_1T)-(\mu_n/m_nT)\big)I & \dots & -\big((\mu_{n-1}/m_{n-1}T)-(\mu_n/m_nT)\big)I \\ 0 & I & \dots & 0 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ 0 & 0 & \dots & I \end{pmatrix} \tag{23}$$

So, the entropy production is rewritten instead of (2), as

$$T\sigma = -\boldsymbol{J}_s \cdot \operatorname{grad} T - \sum_{k=1}^{n-1} \boldsymbol{J}_k \cdot \left[\operatorname{grad}\big((\mu_k/m_k)-(\mu_n/m_n)\big) - \boldsymbol{F}_k + \boldsymbol{F}_n\right] -$$

$$- \dot{\boldsymbol{\Pi}} : (\operatorname{grad} \mathbf{v})^s - \pi \operatorname{div} \mathbf{v} - \sum_{j=1}^{r} J_j A_j \quad , \tag{24}$$

where

$$\boldsymbol{J}_s = (1/T)\Big(\boldsymbol{J}_q - \sum_{k=1}^{n} (\mu_k/m_k)\, \boldsymbol{J}_k\Big) \tag{25}$$

is the entropy flux.

EXPLICIT CALCULATION OF THE DIFFUSION FORCES

From equations (2), (17) and (24), three expressions for the diffusion forces can be written[1, 2, 3] :

$$\boldsymbol{X}_k = -\left[T \operatorname{grad}\big((\mu_k/m_kT)-(\mu_n/m_nT)\big) - \boldsymbol{F}_k + \boldsymbol{F}_n\right] \tag{26}$$

$$\boldsymbol{X}'_k = -\left[\left\{\operatorname{grad}\big((\mu_k/m_k)-(\mu_n/m_n)\big)\right\}_T - \boldsymbol{F}_k + \boldsymbol{F}_n\right] \tag{27}$$

$$\boldsymbol{X}''_k = -\left[\operatorname{grad}\big((\mu_k/m_k)-(\mu_n/m_n)\big) - \boldsymbol{F}_k + \boldsymbol{F}_n\right] \quad . \tag{28}$$

As we can see from these expressions, for computing the diffusion forces, we have to calculate the gradients of the chemical potential. This is made with the aid of the equation of state of our gas mixture.[2, 3]

Let us suppose that we have the virial equation of state:

$$P = kT \sum_{k=1}^{n} (N_k/V) + kT \sum_{k,j=1}^{n} B_{kj}(T)(N_k/V)(N_j/V) +$$

$$+ kT \sum_{k,j,l=1}^{n} B_{kjl}(T)(N_k/V)(N_j/V)(N_l/V) + \ldots \quad , \tag{29}$$

where the B's are functions of T and are symmetric under the interchange of any two index.

Next we will calculate the virial expansion of the chemical potential from the last equation and the relation[2, 4]

$$\mu_k(T, V, N_j\text{'s}) = \mu_k(T, V, N_j\text{'s})_{\text{ideal}} + \int_V^{\infty} \Big((\partial P/\partial N_k)_{T, V', \{N_j\text{'s} \neq k\}} - (kT/V') \Big)\, dV' \tag{30}$$

where

$$\mu_k(T, V, N_j\text{'s})_{\text{ideal}}$$

$$= \int_{T_0}^{T} c_{V,k}\, dT' - T\int_{T_0}^{T} (c_{V,k}\, dT'/T') + kT - kT \ln(V/N_k v_0) + u_{0,k} - T s_{0,k} . \tag{31}$$

In this last equation, $c_{V,k}$ is the specific heat per particle at constant volume of the k component in the ideal gas limit (low densities) and is a function of temperature only; $u_{0,k}$ is the internal energy per particle of the k component in the same limit when $T = T_0$, the standard state temperature; $s_{0,k}$ is the entropy per particle corresponding to this state and v_0 is the volume per particle of the same state.

If we introduce (29) into (30) we obtain

$$\mu_{k}(T,\eta_{j'\mathrm{s}}) = \mu_{k}(T,\eta_{j'\mathrm{s}})_{\mathrm{ideal}} + 2kT\sum_{l} B_{kl}\,\eta_l + {}^3\!/\!_2\, kT \sum_{l,m} B_{klm}\,\eta_l\,\eta_m \; +$$

$$+ \, {}^4\!/\!_3\, kT \sum_{l,m,n} B_{klmn}\,\eta_l\,\eta_m\,\eta_n + \ldots \quad , \tag{32}$$

where the η's are the particle densities of the different components. From this equation we can obtain the virial expansion of the chemical potential gradient:

$$\mathrm{grad}\,\mu_{k} = \{ (\partial\mu_{k\,\mathrm{ideal}}/\partial T)_{\{\eta_{j'\mathrm{s}}\}} + 2k\sum_{l} (TB'_{kl} + B_{kl})\,\eta_l \; +$$

$$+ \, {}^3\!/\!_2\, k \sum_{l,m} (TB'_{klm} + B_{klm})\,\eta_l\,\eta_m + \ldots)\ \mathrm{grad}\ T \; +$$

$$+ \sum_{l} (\partial\mu_{k\,\mathrm{ideal}}/\partial\eta_l)_{T,\{\eta_{j'\mathrm{s}\neq l}\}}\ \mathrm{grad}\ \eta_l + 2kT\sum_{l} B_{kl}\ \mathrm{grad}\ \eta_l \; +$$

$$+ \, 3kT\sum_{l,m} B_{klm}\,\eta_l\ \mathrm{grad}\ \eta_m + \ldots \tag{33}$$

In the case of expression (26) we have to calculate

$$T\ \mathrm{grad}\ (\mu_{k}/m_{k}T) = \mathrm{grad}\ (\mu_{k}/m_{k}) - (\mu_{k}/m_{k}T)\ \mathrm{grad}\ T \quad . \tag{34}$$

On using (31), (32) and (33), the diffusion force $\mathbf{X}_{k}$ is obtained in the following form

$$\mathbf{X}_{k} = -\,[\,\mathrm{grad}\,\big((\mu_{k}/m_{k}) - (\mu_{n}/m_{n})\big) - \big((\mu_{k}/m_{k}) - (\mu_{n}/m_{n})\big)\,(\mathrm{grad}\ T/T) - \mathbf{F}_{k} + \mathbf{F}_{n}\,] \tag{35a}$$

also

$$\mathbf{X}_{k} = [\{(1/T)((u_{n\,\mathrm{ideal}}/m_n) - (u_{k\,\mathrm{ideal}}/m_k)) + 2kT\sum_{l}((B'_{kl}/m_k) - (B'_{nl}/m_n))\,\eta_l +$$

$$+ {}^3\!/_2\, kT\sum_{l,m}((B'_{klm}/m_k) - (B'_{nlm}/m_n))\,\eta_l\,\eta_m + \ldots\}\ \mathrm{grad}\ T + kT((\mathbf{grad}\ \boldsymbol{\eta}_k/m_k\eta_k) -$$

$$-(\mathrm{grad}\ \eta_n/m_n\eta_n)) + 2kT\sum_{l}((B_{kl}/m_k) - (B_{nl}/m_n))\ \mathrm{grad}\ \eta_l +$$

$$+ 3kT\sum_{l,m}((B_{klm}/m_k) - (B_{nlm}/m_n))\,\eta_l\ \mathrm{grad}\ \eta_m - \ldots \mathbf{F}_k + \mathbf{F}_n] \quad , \qquad (35b)$$

where $u_{k\,\mathrm{ideal}}$ is the internal energy per particle of the k component in the ideal gas limit and it is a function of temperature only.

For computing the diffusion force in the form (27), we will use the definition (19) for $(\mathrm{grad}\ \mu_k)_T$. In expression (32) we don't have $\mu_k(T, P, N_{j\text{'s}})$ but $\mu_k(T, V, N_{j\text{'s}})$, so we will use the chain rule for calculating $(\partial\mu_k/\partial T)_{P,\{N_{j\text{'s}}\}}$:

$$(\partial\mu_k/\partial T)_{P,\{N_{j\text{'s}}\}} = (\partial\mu_k/\partial T)_{V,\{N_{j\text{'s}}\}} + (\partial\mu_k/\partial V)_{T,\{N_{j\text{'s}}\}}(\partial V/\partial T)_{P,\{N_{j\text{'s}}\}}, \qquad (36)$$

which can be rewritten as

$$(\partial\mu_k/\partial T)_{P,\{N_{j\text{'s}}\}} = (\partial\mu_k/\partial T)_{V,\{N_{j\text{'s}}\}} +$$

$$+ [(\partial P/\partial T)_{V,\{N_{j\text{'s}}\}}(\partial P/\partial N_k)_{T,V,\{N_{j\text{'s}\neq k}\}}]/(\partial P/\partial V)_{T,\{N_{j\text{'s}}\}} \quad , \qquad (37)$$

where use has been made of the cyclic relation and the Maxwell relation

$$(\partial\mu_k/\partial V)_{T,\{N_{j\text{'s}}\}} = -(\partial P/\partial N_k)_{T,V,\{N_{j\text{'s}\neq k}\}} \qquad (38)$$

Introducing (37) into (19) yields

$$\left(\operatorname{grad}(\mu_k/m_k)\right)_T = \sum_{j=1}^{n} (1/m_k)(\partial\mu_k/\partial\eta_j)_{T,\{\eta_{l\text{'s}}\neq j\}} \operatorname{grad}\eta_j -$$

$$- [\{(\partial P/\partial T)_{\{\eta_{j\text{'s}}\}} (\partial P/\partial N_k)_{T,V,\{N_{j\text{'s}}\neq k\}}\}/m_k(\partial P/\partial V)_{T,\{N_{j\text{'s}}\}}] \operatorname{grad} T \,. \tag{39}$$

So, if a substitution of equations (29), (31), and (32) is made into (39) the diffusion force (27) to second order in the density reads

$$\mathbf{X}'_k = kT\,\{(\operatorname{grad}\eta_n/m_n\eta_n) - (\operatorname{grad}\eta_k/m_k\eta_k)\} +$$

$$+ 2kT\sum_j \left((B_{nj}/m_n) - (B_{kj}/m_k)\right) \operatorname{grad}\eta_j +$$

$$+ 3kT\sum_{l,j} \left((B_{nlj}/m_n) - (B_{klj}/m_k)\right) \eta_l \operatorname{grad}\eta_j + \ldots + k[\left((1/m_n) - (1/m_k)\right) +$$

$$+ 2\sum_l \left((B_{nl}/m_n) - (B_{kl}/m_k)\right)\eta_l + (1/\eta)\left((1/m_n) - (1/m_k)\right)\sum_{j,l}(TB'_{jl} - B_{jl})\eta_j\eta_l +$$

$$+ 3\sum_{j,l}\left((B_{njl}/m_n) - (B_{kjl}/m_k)\right)\eta_j\eta_l +$$

$$+ (1/\eta)\left((1/m_n) - (1/m_k)\right)\sum_{j,l,m}(-2B_{jlm} + TB'_{jlm})\eta_j\eta_l\eta_m +$$

$$+ (2/\eta)\sum_j\left((B_{nj}/m_n) - (B_{kj}/m_k)\right)\eta_j\sum_{l,m}(-B_{lm} + TB'_{lm})\eta_l\eta_m -$$

$$- (2/\eta^2)\left((1/m_n) - (1/m_k)\right)\sum_{j,l}(TB'_{jl} - B_{jl})\eta_j\eta_l\sum_{p,q}B_{pq}\eta_p\eta_q + \ldots] \operatorname{grad} T +$$

$$+ \mathbf{F}_k - \mathbf{F}_n \tag{40}$$

Finally, the 3th form of the diffusion forces (28) is obtained directly from equations (33) and (31), leaving the following expression

$$
\begin{aligned}
\mathbf{X}''_k = \{ & [\int_{T_0}^{T} ((c_{V,k}/m_k) - (c_{V,n}/m_n))(dT'/T')]_{\text{ideal}} - k((1/m_k) - (1/m_n)) - \\
& - k((1/m_k) - (1/m_n)) \ln v_0 - k((\ln \eta_k/m_k) - (\ln \eta_n/m_n)) + ((s_{0,k}/m_k) - (s_{0,n}/m_n)) - \\
& - 2k \sum_l [T((B'_{kl}/m_k) - (B'_{nl}/m_n)) + ((B_{kl}/m_k) - (B_{nl}/m_n))] \eta_l - \\
& - \tfrac{3}{2} k \sum_{l,m} [T((B'_{klm}/m_k) - (B'_{nlm}/m_n)) + ((B_{klm}/m_k) - (B_{nlm}/m_n))] \eta_l \eta_m - \dots \} \times \\
& \times \operatorname{grad} T - kT((\operatorname{grad} \eta_k/m_k \eta_k) - (\operatorname{grad} \eta_n/m_n \eta_n)) - \\
& - 2kT \sum_j ((B_{kj}/m_k) - (B_{nj}/m_n)) \operatorname{grad} \eta_j - \\
& - 3kT \sum_{l,m} ((B_{klm}/m_k) - (B_{nlm}/m_n)) \eta_l \operatorname{grad} \eta_m - \dots + \mathbf{F}_k - \mathbf{F}_n \qquad (41)
\end{aligned}
$$

BINARY MIXTURE

In case we have a mixture of two components only, the matrix (15) which transforms the fluxes is then given by

$$\mathbf{B} = \begin{pmatrix} I & -\boldsymbol{H} I \\ 0 & I \end{pmatrix} , \qquad (42)$$

where

$$\boldsymbol{H} = (\mathbf{H}_1/m_1) - (\mathbf{H}_2/m_2) \quad . \qquad (43)$$

The new vectorial fluxes are then

$$\boldsymbol{J}' = \begin{pmatrix} \boldsymbol{J}_q' \\ \boldsymbol{J}_1 \end{pmatrix} = \begin{pmatrix} \boldsymbol{J}_q - \boldsymbol{H}\boldsymbol{J}_1 \\ \boldsymbol{J}_1 \end{pmatrix} \quad , \tag{44}$$

and the corresponding thermodynamical forces, when there are no external forces present, are given by

$$\boldsymbol{X}' = \begin{pmatrix} -(\mathrm{grad}\, T/T) \\ -(\mathrm{grad}\, \mu)_T \end{pmatrix} \quad , \tag{45}$$

where we have defined the chemical potential of the mixture as

$$\mu = (\mu_1/m_1) - (\mu_2/m_2) \quad . \tag{46}$$

The new matrix of phenomenological coefficients (11) transforms into

$$\mathbf{L}' = \begin{pmatrix} (L_{qq} - 2\boldsymbol{H}\, L_{1q} + \boldsymbol{H}^2 L_{11})\, I & (L_{1q} - \boldsymbol{H}\, L_{11})\, I \\ (L_{1q} - \boldsymbol{H}\, L_{11})\, I & L_{11}\, I \end{pmatrix} \quad , \tag{47}$$

If we use (21), (22) and the fact that the chemical potential is an intensive quantity, we have

$$\boldsymbol{H} = \mu - T\,(\partial\mu/\partial T)_{P,\{N_1,N_2\}} = \mu - T\,(\partial\mu/\partial T)_{P,c} \tag{48}$$

where c is the concentration of the component $1(c_{\boldsymbol{k}} = \rho_{\boldsymbol{k}}/\rho;\ \boldsymbol{k} = 1,2)$.

Now we will define[5] D, k_T and κ by means of the following equations

$$L_{11} = \rho D/(\partial\mu/\partial c)_{T,P} \tag{49}$$

$$L_{1q} = \rho D\{[(\mu - T\,(\partial\mu/\partial T)_{P,c})/(\partial\mu/\partial c)_{T,P}] + k_T\} \tag{50}$$

$$L_{qq} = \kappa T + [\rho D \{\mu - T(\partial\mu/\partial T)_{P,c} + k_T(\partial\mu/\partial c)_{T,P}\}^2]/(\partial\mu/\partial c)_{T,P} \tag{51}$$

An introduction of (48), (49), (50) and (51) into (47) leaves the new matrix of phenomenological coefficients as

$$\mathbf{L}' = \begin{pmatrix} [\kappa T + k_T^2 \rho D(\partial\mu/\partial c)_{T,P}]\, I & [\rho D k_T]\, I \\ [\rho D k_T]\, I & [\rho D/(\partial\mu/\partial c)_{T,P}]\, I \end{pmatrix} \tag{52}$$

then the new linear relations (11) can be written as

$$\begin{aligned} &\boldsymbol{J}_q - (\mu - T(\partial\mu/\partial T)_{P,c})\boldsymbol{J}_1 \\ &= -(\kappa T + k_T^2 \rho D(\partial\mu/\partial c)_{T,P} - k_T \rho D T(\partial\mu/\partial T)_{P,c})(\text{grad } T/T) - \\ &\quad - \rho D k_T \text{ grad } \mu \end{aligned} \tag{53}$$

$$\begin{aligned} \boldsymbol{J}_1 &= -\rho D[k_T - T(\partial\mu/\partial T)_{P,c}/(\partial\mu/\partial c)_{T,P}](\text{grad } T/T) - \\ &\quad - [\rho D/(\partial\mu/\partial c)_{T,P}] \text{ grad } \mu . \end{aligned} \tag{54}$$

It is convenient to eliminate grad μ from the expression for the heat flux, replacing it by $\boldsymbol{J}_1$ and grad T. Then we have

$$\boldsymbol{J}_q = [\mu - T(\partial\mu/\partial T)_{P,c} + k_T(\partial\mu/\partial c)_{T,P}]\boldsymbol{J}_1 - \kappa \text{ grad } T . \tag{55}$$

The other independent equation shall be obtained from (54) using the fact that $\mu = \mu(T, P, c)$.

$$\mathbf{J}_1 = -\rho D\,[\,\text{grad}\; c + k_T\,(\text{grad}\; T/T) + k_P\,(\text{grad}\; P/P]\;, \tag{56}$$

where we have made

$$k_P = P\,(\partial\mu/\partial P)_{c,T}/(\partial\mu/\partial c)_{P,T}\;. \tag{57}$$

The coefficient D is called the diffusion coefficient or mass transfer coefficient; it gives the diffusion flux when only a concentration gradient is present. The diffusion flux due to the temperature gradient is given by the thermal diffusion coefficient $k_T D$; the dimensionless quantity k_T is called the thermal diffusion ratio.

The last term in (56) has to be taken into account only when there is a considerable pressure gradient in the fluid. The coefficient $k_P D$ may be called the barodiffusion coefficient. It should be noticed that, by formula (57), the dimensionless quantity k_P is entirely determined by thermodynamic properties alone. Moreover, for $\mathbf{J}_1 = 0$ in equation (55), we have

$$\mathbf{J}_q = -\,\kappa\;\text{grad}\; T \tag{58}$$

so that κ is just the thermal conductivity.

Having in mind that D, $k_T D$ and κ are the coefficients most easily obtained by experimental methods, we can get from them the tensor of phenomenological coefficients that relates fluxes and forces of vectorial character in the standard form[1]. The equations that we will use are then (49), (50) and (51).

Now, we shall obtain the expressions μ, $(\partial\mu/\partial T)_{P,c}$ and $(\partial\mu/\partial c)_{T,P}$ that appear in formulae (49)(50) and (51). Again, we will suppose that in the equation of state, it is easier to have the pressure as a function of temperature and the particle densities. As an example, we will take the virial equation of state (29) and the chemical potential (32), which, expressed as a function of the temperature, specific volume and concentration of the components 1 and 2, gives us

$$P = (kT/V)\sum_{k=1}^{2}(c_k/m_k) + (kT/V^2)\sum_{k,j=1}^{2} B_{kj}\,(c_k/m_k)(c_j/m_j)\; +$$

$$+\,(kT/V^3)\sum_{k,j,l=1}^{2} B_{kjl}(c_k/m_k)(c_j/m_j)(c_l/m_l) + \ldots \tag{59}$$

$$\mu_k = [\int_{T_0}^{T} c_{V,k}\, dT' - T\int_{T_0}^{T} (c_{V,k}\, dT'/T')]_{\text{ideal}} + kT + kT \ln (v_0/m_k V) +$$

$$+ kT \ln c_k + u_{0,k} - T s_{0,k} + (2kT/V) \sum_{l=1}^{2} B_{kl} (c_l/m_l) +$$

$$+ 3/2\, (kT/V^2) \sum_{l,m=1}^{2} B_{klm} (c_l/m_l)(c_m/m_m) + \ldots \tag{60}$$

In the last equation we don't have $\mu_k(T, P, c)$ but $\mu_k(T, V, c)$, so we shall use again the chain rule for calculating the partial derivatives of the chemical potential when the pressure is constant. In this way we obtain

$$(\partial\mu/\partial T)_{P,c} = (\partial\mu/\partial T)_{V,c} + [(\partial P/\partial T)_{V,c} (\partial P/\partial c)_{T,V} /(\partial P/\partial V)_{T,c}] \tag{61}$$

$$(\partial\mu/\partial c)_{T,P} = (\partial\mu/\partial c)_{T,V} + [(\partial P/\partial c)^2_{T,V} /(\partial P/\partial V)_{T,c}] \,. \tag{62}$$

On obtaining these last two expressions, use has been made of the cyclic relation and the Maxwell relation:

$$(\partial\mu/\partial V)_{T,c} = - (\partial P/\partial c)_{T,V} \,. \tag{63}$$

From (60), we can have the chemical potential of the mixture (46) as

$$\begin{aligned}
\mu = (\mu_1/m_1) - (\mu_2/m_2) = {} & [(1/m_1)\int_{T_0}^{T} c_{V,1}\, dT' - (1/m_2)\int_{T_0}^{T} c_{V,2}\, dT']_{\text{ideal}} - \\
& - [(T/m_1)\int_{T_0}^{T} (c_{V,1}\, dT'/T') - (T/m_2)\int_{T_0}^{T} (c_{V,2}\, dT'/T']_{\text{ideal}} + \\
& + kT\big((1/m_1) - (1/m_2)\big)\big(1 + \ln(v_0/V)\big) - kT\big((\ln m_1/m_1) - (\ln m_2/m_2)\big) + \\
& + kT\big((\ln c_1/m_1) - (\ln c_2/m_2)\big) + \big((u_{0,1}/m_1) - (u_{0,2}/m_2)\big) - \\
& - T\big((s_{0,1}/m_1) - (s_{0,2}/m_2)\big) + (2kT/V)\sum_{l}\big((B_{1l}/m_1) - (B_{2l}/m_2)\big)(c_l/m_l) + \\
& + 3/2\,(kT/V^2)\sum_{l,m}\big((B_{1lm}/m_1) - (B_{2lm}/m_2)\big)(c_l/m_l)(c_m/m_m) + \dots \qquad (64)
\end{aligned}$$

If we introduce (59) and (64) into (61) and (62), then we have, to second order in the density

$$\begin{aligned}
(\partial\mu/\partial T)_{P,c} = {} & - [\int_{T_0}^{T}(1/T')\big((c_{V,1}/m_1) - (c_{V,2}/m_2)\big)\, dT']_{\text{ideal}} + \\
& + k\big((1/m_1) - (1/m_2)\big)\ln v_0 - \big((s_{0,1}/m_1) - (s_{0,2}/m_2)\big) + k\big((\ln\eta_1/m_1) - (\ln\eta_2/m_2)\big) + \\
& + 2k\sum_{l}\big((TB'_{1l}/m_1) - (TB'_{2l}/m_2)\eta_l - k\big((1/m_1) - (1/m_2)\big)\sum_{l,m}(TB'_{lm} - B_{lm})(\eta_l\eta_m/\eta) \\
& - 2k\sum_{l}\big((B_{1l}/m_1) - (B_{2l}/m_2)\big)\eta_l\sum_{p,m}(TB'_{pm} - B_{pm})(\eta_p\eta_m/\eta) + \\
& + 2k\big((1/m_1) - (1/m_2)\big)\sum_{k,j}B_{kj}(\eta_k\eta_j/\eta)\sum_{l,m}(TB'_{lm} - B_{lm})(\eta_l\eta_m/\eta) + \\
& + 3/2\,k\sum_{l,m}[\big((TB'_{1lm} - B_{1lm})/m_1\big) - \big((TB'_{2lm} - B_{2lm})/m_2\big)]\,\eta_l\eta_m - \\
& - k\big((1/m_1) - (1/m_2)\big)\sum_{l,m,p}(TB'_{lmp} - 2B_{lmp})(\eta_l\eta_m\eta_p/\eta) + \dots \qquad (65)
\end{aligned}$$

$$
\begin{aligned}
(\partial\mu/\partial c)_{T,P} &= (kT/V)\,\{((1/m_1^2\eta_1) + (1/m_2^2\eta_2)) + \\
&+ 2((B_{11}/m_1^2) - (2B_{12}/m_1m_2) + (B_{22}/m_2^2)) + \\
&+ 3\sum_l ((B_{11l}/m_1^2) - (2B_{12l}/m_1m_2) + (B_{22l}/m_2^2))\,\eta_l - (1/\eta)((1/m_1) - (1/m_2))^2 - \\
&- (4/\eta)((1/m_1) - (1/m_2)) \sum_j ((B_{1j}/m_1) - (B_{2j}/m_2))\,\eta_j + \\
&+ (2/\eta^2)((1/m_1) - (1/m_2))^2 \sum_{k,j} B_{kj}\eta_k\eta_j + (8/\eta^2)((1/m_1) - (1/m_2)) \times \\
&\times \sum_j ((B_{1j}/m_1) - (B_{2j}/m_2))\eta_j \sum_{k,l} B_{kl}\eta_k\eta_l - (4/\eta)\,[\sum_j ((B_{1j}/m_1) - (B_{2j}/m_2))\,\eta_j]^2 - \\
&- (6/\eta)((1/m_1) - (1/m_2)) \sum_{k,j} ((B_{1kj}/m_1) - (B_{2kj}/m_2))\,\eta_k\eta_j + \\
&+ (3/\eta^2)((1/m_1) - (1/m_2))^2 \times \sum_{k,j,l} B_{kjl}\eta_k\eta_j\eta_l - (4/\eta^3)((1/m_1) - (1/m_2))^2 \times \\
&\times [\sum_{k,j} B_{kj}\eta_k\eta_j]^2 + \ldots\} \quad . \qquad (66)
\end{aligned}
$$

And, on substituting equations (64), (65) and (66) into (49), (50) and (51), we can have the coefficients which relate the fluxes and forces of vectorial character as a function of temperature and particle densities and also as a function of the experimental quantities D, k_T and κ.

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RESUMEN

Las diferentes selecciones de flujos y las fuerzas termodinámicas correspondientes se escriben dentro de la teoría lineal de la termodinámica irreversible. En este artículo se presenta un método para calcular explícitamente estas fuerzas por medio de la ecuación de estado de nuestra mezcla de gas. También se obtendrán los coeficientes fenomenológicos de las leyes lineales en su forma usual, como función de algunos coeficientes fácilmente obtenibles por métodos experimentales, usando de nuevo la ecuación de estado de la mezcla de gas. Esto último se analizará sólo para una mezcla binaria.