

COMPARISON OF MASS AND HEAT TRANSPORT IN FLUID AND MEMBRANE SYSTEMS

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Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary

Abstract

The interrelations between empirical mass and heat transport coefficients (diffusion, pressure diffusion, thermal diffusion and sedimentation coefficients; Dufour, pressure and sedimentation thermal coefficients, thermal conductivity) are discussed for continuous binary membrane systems using Irreversible Thermodynamics and compared with those of binary fluid systems. It is shown that only three coefficients are independent and that in the membrane relations the factor representing the buoyancy effect (mass or volume correction) is absent; because these systems are always in mechanical equilibrium, while in fluid systems in general no mechanical restrictions exist. This feature determines important differences between both types of systems in the case of mass and heat transports due to forces involved in the mechanical balance, differences which are discussed in detail. On the other hand, the properties of the coefficients of transport processes due to concentration and/or temperature gradients are essentially the same in both types of systems.

Resumen

Las relaciones entre los coeficientes empíricos de transporte de masa y de calor (coeficientes de difusión, de difusión por presión, de termodifusión, de sedimentación, de Dufour, coeficientes térmicos por presión y por sedimentación y conductividad térmica) se analizan para sistemas de membranas binarios continuos mediante la Termodinámica de los Procesos Irreversibles y se comparan con las correspondientes a sistemas fluidos binarios. Se demuestra que sólo tres coeficientes son independientes y que en las relaciones para membranas no aparece el factor correspondiente al empuje de Arquímedes (correcciones por masa o por volumen), pues estos sistemas están siempre en equilibrio mecánico, mientras que para sistemas fluidos no existen, en general, restricciones mecánicas. Esta característica determina importantes diferencias entre ambos tipos de sistemas en el caso de transportes de masa y de calor originados por fuerzas incluidas en el balance mecánico, diferencias que se discuten en detalle. Por otra parte, las propiedades de los coeficientes de los procesos de transporte debidos a gradientes de concentración y/o de temperatura son esencialmente las mismas para ambos tipos de sistemas.

Introduction

Concentration, pressure and/or temperature gradients as well as a gravitational or centrifugal force field originate transport of matter and of heat by direct and cross effects. These processes may be described by empirical transport coefficients as well as by phenomenological transport coefficients of Irreversible Thermodynamics. Furthermore, the thermodynamic phenomenological description allows stating the interrelations between the empirical coefficients, as the number of these is in general greater than the number of independent phenomenological coefficients and also in terms of the Onsager Reciprocal Relations (ORR). In fluid systems, gaseous or liquid, the transport analysis has been given by Haase [1]. In this paper we present the analysis for continuous membrane systems. The fundamental difference is that in fluid systems no mechanical restrictions exist while in the interior of a membrane system a force balance (mechanical equilibrium) must be taken into account [2,3]. This differentiating aspect has been previously taken [4] into consideration for the formulation of the general relation between permeability and the diffusion coefficient. The treatment is now extended to other transport coefficients improving an earlier description also due to Haase [5]. It is shown that the characteristics of the transport coefficients related to processes due to driving forces involved in the mechanical balance (pressure gradient and the centrifugal or gravitational field) are different in both types of systems, while those coefficients related to forces not connected by the mechanical equilibrium condition (concentration and temperature gradients) are essentially the same in these systems.

For simplicity only systems with two uncharged components will be discussed, i.e. binary (gaseous or liquid) fluid mixtures and binary continuous membrane systems consisting of the membrane substance and the permeating substance which forms the pure fluid (gas or liquid) phases outside the membrane. In the following Section the treatment given by Haase [1] for transport processes in fluid systems is reviewed, next, processes inside the membrane systems are analysed, while in the subsequent section the comparison is made and final results presented and discussed.

Transport processes in fluid systems

In the general situation, without any mechanical restrictions, in binary fluid systems the molar fluxes ${}_v J_i$ ($i = 1, 2$) must be stated in the barycentric reference frame (index v) and only one flux is independent. Following Haase [1] we write the *empirical* flow equations for the mass flow ${}_v J_2$ for component 2 and for the heat flux J_q as follows:

$$x_1 \bar{V} \cdot {}_v J_2 = - \left(\frac{\rho_1}{\rho} \right) \left[\underset{\text{diffusion}}{D \cdot \text{grad} x_2} + \underset{\text{pressure diffusion}}{\frac{D_P}{P} \cdot \text{grad} P} - \underset{\text{thermo-diffusion}}{\frac{D_T}{T} \cdot \text{grad} T} \right] \quad (1)$$

$$J_q = - [\lambda_c \cdot \text{grad} x_2 + \lambda_p \cdot \text{grad} P + \lambda_o \cdot \text{grad} T] \quad (2)$$

Dufour effect	pressure thermal effect	thermal conduction
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Equations (1)-(2) include *six* transport processes, each of which is characterised by one *empirical* transport coefficient. The denomination of the different transport processes is indicated below each term, denomination that also applies to the corresponding empirical transport coefficient. x_i is the mole fraction of component i , \bar{v} the molar volume of the system, ρ_i the partial density of i , ρ the density of the system, P the pressure and T the thermodynamic temperature. This scheme does not exclude the external force fields mentioned in the Introduction. Their influence does not appear explicitly in the formulas as they act, as it will be shown below, through a contribution to the pressure gradient.

On the other hand, the fluxes and forces of the *phenomenological* description are determined by the *dissipation* function, which reads for the transport processes at hand as follows [1]:

$$\Psi = \sum_v J_i \cdot X_i + \sum_v J_2 \cdot X_2 + J_q \cdot X_q \quad (>0) \tag{3}$$

The general forces X_i ($i = 1, 2$) and X_q are defined as [1]

$$X_i = M_i (g + \Omega^2 \cdot r) + F_i - V_i \cdot \text{grad}P - \text{grad}_{T,P} \mu_i \tag{4}$$

$$X_q = -\frac{1}{T} \cdot \text{grad}T \tag{5}$$

Here M_i is the molar mass of i , V_i the partial molar volume, μ_i the chemical potential and F_i a molar external mechanical force acting on component i , g the gravitational acceleration, Ω the angular velocity of the centrifuge and r the distance to the rotation axis. $\text{grad}_{T,P}$ indicates a isothermal-isobaric gradient.

The barycentric fluxes $\sum_v J_i$ in (1) and (3) are given by

$$\sum_v J_i = c_i (v_i - v) \tag{6}$$

with

$$\rho \cdot v = \rho_1 \cdot v_1 + \rho_2 \cdot v_2, \tag{7}$$

where c_i is the molar volume concentration (molarity) of i , v_i and v are the local velocity of i and the local barycentric velocity, respectively, and $\rho_i (= c_i M_i)$ the partial density of i . Because of (7) these fluxes not independent,

$$M_1 \sum_v J_1 + M_2 \sum_v J_2 = 0, \tag{8}$$

and inserting (8) in (3) the dissipation function ψ takes the form

$$\Psi = \sum_v J_2 \cdot \sum_v X_2 + J_q \cdot X_q \quad (>0) \tag{9}$$

This expression defines independent flows and forces for the present case. $\sum_v X_2$ is the conjugated barycentric molar force of the independent flux $\sum_v J_2$:

$$\sum_v X_2 \equiv X_2 - \frac{M_2}{M_1} \cdot X_1 \tag{10}$$

In fluid systems no additional mechanical forces act on the components, i.e.

$$F_1 = 0 \quad , \quad F_2 = 0 \quad , \tag{11}$$

and inserting with this condition equation (4) in (10) gives the general expression of $\sum_v X_2$:

$${}_v X_2 = -\frac{\rho}{\rho_1} \left[\left(V_2 - \frac{M_2}{\rho} \right) \cdot \text{grad} P + \text{grad}_{T,P} \mu_2 \right] \quad (12)$$

In the derivation of (12) the following thermodynamic relations have been used:

$$\rho_i = c_i M_i \quad , \quad \rho = \rho_1 + \rho_2 \quad (13a)$$

$$c_1 V_1 + c_2 V_2 = 1 = \rho_1 V_1 / M_1 + \rho_2 V_2 / M_2 \quad (13b)$$

$$c_1 \text{grad}_{T,P} \mu_1 + c_2 \text{grad}_{T,P} \mu_2 = 0 \quad (13c)$$

$$\text{grad}_{T,P} \mu_2 = \mu_{22}^{(x)} \cdot \text{grad} x_2 \quad \text{with} \quad \mu_{22}^{(x)} \equiv \left(\frac{\partial \mu_2}{\partial x_2} \right)_{T,P} (> 0) \quad (13d)$$

Equations (13c)-(13d) state important thermodynamic properties. Equation (13c) is the Gibbs-Duhem relation and the condition $\mu_{22}^{(x)} > 0$ of (13d) states the material phase stability condition in binary systems.

Equation (9) states as independent fluxes ${}_v J_2$ and J_q and as conjugated independent general forces ${}_v X_2$ and X_q . The *phenomenological* flow equations are therefore:

$${}_v J_2 = a_{22} \cdot {}_v X_2 + a_{2q} \cdot X_q \quad (14)$$

$$J_q = a_{q2} \cdot {}_v X_2 + a_{qq} \cdot X_q \quad (15)$$

where a_{jk} ($j, k = 2, q$) are the *barycentric phenomenological* coefficients. Equations (14)-(15) include *four* coefficients; two are *direct* coefficients (a_{22} , a_{qq}) and the other two are *coupling* (or cross) coefficients (a_{2q} , a_{q2}). For these coefficients the following inequalities are valid [1]:

$$a_{22} > 0, \quad a_{qq} > 0, \quad a_{22} \cdot a_{qq} > a_{2q} \cdot a_{q2}, \quad (16)$$

inequalities, which derive from the positive condition of the dissipation function ψ , equation (9). Moreover, the cross coefficients follow the *Onsager Reciprocity Relation* (ORR):

$$a_{2q} = a_{q2} \quad . \quad (17)$$

Thus, three of these four phenomenological coefficients are independent.

By insertion of (5) and (12) in (14)-(15) and taking (13) into account the coefficients of (1)-(2) and of (14)-(15) may be related. The results are given in Table 1.

In the foregoing description the presence of a gravitational or centrifugal field is allowed by (4), but its effect cancels in (12). For characterising the mass and heat transports in the sedimentation process the analysis has to be made in condition of *mechanical equilibrium* [6]. The force balance vanish under these circumstances:

$$c_1 X_1 + c_2 X_2 = 0 = \rho (g + \Omega^2 r) - \text{grad} P \quad \Rightarrow \quad \rho (g + \Omega^2 r) = \text{grad} P \quad (18)$$

(mechanical equilibrium)

where (4) and (13) have been used. Equation (18) shows that the general effect of the presence of an external force field is to create, in a continuous system in mechanical equilibrium, a pressure gradient. Since we are only interested in the relation between transport coefficients we will analyse the sedimentation process only at isothermal ($\text{grad} T = 0$) and at initial ($t=0$, $\text{grad} x_2 = 0$) conditions (For other details see [1]). For this situation the flow equations (1)-(2) and (14)-(15), taking (18) into account, are:

$$\begin{aligned}
x_1 \bar{V} \cdot v \cdot J_2 (\text{grad}T = 0, \text{grad}_{T,P} \mu_2 = 0, t = 0) &= \frac{\rho_1 c_2 s_2}{\rho c_1 V_1} (g + \Omega^2 r) = \\
&= - \left(V_2 - \frac{M_2}{\rho} \right) \frac{\rho_1}{\rho} \cdot a_{22} \cdot \rho (g + \Omega^2 r)
\end{aligned} \tag{sedimentation} \quad (19)$$

$$\begin{aligned}
J_q (\text{grad}T = 0, \text{grad}_{T,P} \mu_2 = 0, t = 0) &= \lambda_s (g + \Omega^2 r) = \\
&= - \left(V_2 - \frac{M_2}{\rho} \right) \frac{\rho_1}{\rho} \cdot a_{q2} \cdot \rho (g + \Omega^2 r)
\end{aligned} \tag{sedimentation thermal effect} \quad (20)$$

In these equations the first expression corresponds to the empirical formulation, defining the corresponding empirical transport coefficients, and the second expression corresponds to the phenomenological formulation. In equation (19) s_2 is the *sedimentation* coefficient of component 2 and equation (19) responds to the usual formulation in the literature [6]. On the other hand, equation (20) serves as the introduction and definition of the *sedimentation thermal effect* and its coefficient λ_s , effect not described so far in the literature; its existence is a natural prediction of Irreversible Thermodynamics. Haase [1] did not consider the sedimentation process in the present context, i.e. in non-isothermal conditions. Equations (19) and (20) allow to derive the interpretation of s_2 and λ_s , respectively, in terms of the phenomenological coefficients a_{22} and a_{q2} . These results are included in Table 1.

In conclusion, for binary fluid systems of uncharged species and taking the ORR (equation 17) into account, *three* independent phenomenological coefficients interpret all the transport processes, which are described by *eight* empirical coefficients. Thus there must exist *five* independent relations among the empirical coefficients, relations that are analysed in a subsequent section.

Transport processes in binary membrane systems.

Let us now consider the same transport processes as in the preceding section, but in the inside of a binary membrane system. Component 1 is now the membrane substance forming the membrane matrix and component 2 is the mobile permeant, which forms the pure (gas or liquid) phases outside the membrane. As has been pointed out by Schmitt and Craig [2] and also by Silverberg [3] for a membrane exposed to external mechanical forces there must also exist another mechanical force acting through the supporting frame which counterbalance the former external forces and which is needed to restrain the membrane from moving. Thus within the membrane there exists always a mechanical equilibrium, as the mechanical response of the supporting frame adjusts itself in terms of the applied forces. The mechanical reaction of the frame acts only on the membrane substance, i.e. on the matrix, and not on the other components of the membrane system; hence

$$F_1 \neq 0 \quad , \quad F_2 = 0 \quad , \tag{21}$$

Equation (21) establishes the difference with the fluid systems (eq.11). With (4) and (21) the mechanical balance condition in membrane systems becomes

$$c_1 X_1 + c_2 X_2 = 0 = \rho (g + \Omega^2 r) + c_1 F_1 - \text{grad}P \quad \Rightarrow \quad \rho (g + \Omega^2 r) + c_1 F_1 = \text{grad}P \tag{22}$$

(mechanical equilibrium in membrane systems)

where (13) has been used. Equation (22) shows that within the membrane systems the sedimentation force and the pressure gradient are independent from each other, in direct contraposition to fluid systems (equation 18).

Table 1 Relations between empirical and phenomenological coefficients

<i>Fluid systems</i>	<i>Process</i>	<i>Membrane systems</i>
a) $D = x_1 \bar{V} \mu_{22}^{(x)} \cdot \left(\frac{\rho}{\rho_1} \right)^2 \cdot a_{22}$	diffusion	a') $D' = x_1 \bar{V} \cdot \mu_{22}^{(x)} \cdot L_{22}$
b) $\frac{D_p}{P} = x_1 \bar{V} \left(V_2 - \frac{M_2}{\rho} \right) \left(\frac{\rho}{\rho_1} \right)^2 \cdot a_{22}$	pressure diffusion	b') $\frac{D'_p}{P} = x_1 \bar{V} \cdot V_2 \cdot L_{22}$
c) $s_2 = c_1 \bar{V} \cdot (M_2 - \rho V_2) \left(\frac{\rho}{\rho_1} \right)^2 \cdot \frac{a_{22}}{c_2}$	sedimentation	c') $s'_2 = c_1 \bar{V} \cdot M_2 \cdot \frac{L_{22}}{c_2}$
d) $\frac{D_T}{T} = -x_1 \bar{V} \cdot \left(\frac{\rho}{\rho_1} \right) \cdot \frac{a_{22}}{T}$	thermodiffusion	d') $\frac{D'_T}{T} = -x_1 \bar{V} \cdot \frac{L_{22}}{T}$
e) $\lambda_c = -\mu_{22}^{(x)} \cdot \left(\frac{\rho}{\rho_1} \right) \cdot a_{q2}$	Dufour effect	e') $\lambda'_c = -\mu_{22}^{(x)} \cdot L_{q2}$
f) $\lambda_p = \left(V_2 - \frac{M_2}{\rho} \right) \left(\frac{\rho}{\rho_1} \right) \cdot a_{q2}$	pressure thermal effect	f') $\lambda'_p = V_2 \cdot L_{q2}$
g) $\lambda_s = (M_2 - \rho V_2) \left(\frac{\rho}{\rho_1} \right) \cdot a_{q2}$	sedimentation thermal effect	g') $\lambda'_s = M_2 \cdot L_{q2}$
h) $\lambda_o = a_{qq} / T$	thermal conduction	h') $\lambda'_o = L_{qq} / T$

This differentiating aspect was not taken into account in the thermodynamic-phenomenological theory of permeation and thermo osmosis originally formulated by Haase [5], but it has been afterwards introduced and used to derive the general relationship between the permeability and the diffusion coefficient [4]. Let us now extend this treatment to the other transport phenomena.

In membrane processes the mass fluxes are referred to the membrane matrix (index 1) and the *empirical* flow equations read now [5]:

$$x_1 \bar{V}_1 J_2 = -D' \cdot \text{grad} x_2 + \frac{D'_p}{P} \cdot \text{grad} P - \frac{D'_T}{T} \cdot \text{grad} T + c_2 s'_2 \frac{\bar{V}^2}{V_1} (g + \Omega^2 r) \quad (23)$$

diffusion
pressure diffusion
thermo-diffusion
sedimentation

$$J_q = -\lambda'_c \cdot \text{grad}x_2 - \lambda'_p \cdot \text{grad}P + \lambda'_s (g + \Omega^2 r) - \lambda'_o \cdot \text{grad}T \tag{24}$$

Dufour effect	pressure thermal effect	sedimentation thermal effect	thermal conduction
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As in equations (1)-(2) each term in equations (23)-(24) defines the corresponding empirical transport coefficient, which for membranes is distinguished with a prime ('). In equations (23)-(24) the terms corresponding to sedimentation are directly included as a straightforward consequence of equation (22), terms which were not considered in the theory developed by Haase [5].

From the phenomenological point of view the dissipation function ψ is still given by equation (9), but in addition to the relation among mass flows (eq.8) we have now also a relation among forces given by equation (22). In mechanical equilibrium ψ becomes independent of the reference systems used for the mass fluxes (Prigogine's theorem [7]) and it is convenient to express the independent mass flow of component 2 directly respect to the membrane (index 1). Thus with (22) equation (9) becomes:

$$\Psi = {}_1J_{2,1}X_2 + J_q \cdot X_q \quad (>0) \tag{25}$$

where ${}_1J_2 = c_2(v_2 - v_1)$ (a) ${}_1X_2 = X_2$ (b) (26)

It is readily shown that these membrane-fixed quantities are related to the barycentric quantities by

$${}_1J_2 = (\rho/\rho_1) {}_vJ_2 \quad (a) \quad {}_1X_2 (= X_2) = (\rho_1/\rho) {}_vX_2 \quad (b) \tag{27}$$

Here equations (6)-(8), (10), (13) and (22) have been used. With (27) Prigogine's theorem is readily verified.

Equation (25) states that the conjugated force (${}_1X_2$) corresponding to the flux ${}_1J_2$ is directly X_2 (equation 26b), which by (21) and (4) takes the simple following form:

$$X_2 (= {}_1X_2) = M_2 (g + \Omega^2 r) - V_2 \text{grad}P - \mu_{22}^{(x)} \text{grad}x_2 \tag{28}$$

and the corresponding phenomenological flow equations are

$${}_1J_2 = L_{22} \cdot X_2 + L_{2q} \cdot X_q \tag{29}$$

$$J_q = L_{q2} \cdot X_2 + L_{qq} \cdot X_q \tag{30}$$

L_{ik} (i, k = 2, q) are the *four* phenomenological coefficients of the present case, taken relative to the membrane. These coefficients have similar properties to the barycentric ones. They follow the ORR,

$$L_{2q} = L_{q2} \quad , \tag{31}$$

and the same inequalities [1],

$$L_{22} > 0, \quad L_{qq} > 0, \quad L_{22} \cdot L_{qq} > L_{2q} \cdot L_{q2}, \tag{32}$$

By substitution of (5) and (28) in equations (29)-(30) these equations may be compared with the empirical equations (23)-(24). The relations among coefficients are also given in Table 1. Again, as in the case of fluid systems; *three* independent phenomenological coefficients describe all the transport processes within binary membrane systems of uncharged components, processes that are also represented by *eight* empirical coefficients. Thus here also *five* independent relations must exist among

these coefficients, relations that are outlined in the next section.

It is important to point out that although the force F_1 is of primary significance for the formulation of the description of the transport processes in membrane systems this force does not appear explicitly neither in the empirical flow equations nor in the phenomenological ones and therefore there does not exist any exigency to characterise F_1 with more physical details. In other words, only the acceptance of its existence is essential. Further consequences of this will be considered later on.

Relationships among the transport coefficients

In Table 1 the relations between empirical transport coefficients and the corresponding phenomenological coefficients in both types of systems are given. The formulas contained in both sections of this table may be directly compared if the relations between the phenomenological coefficients in the barycentric frame and in the membrane fixed frame are taken into account. These relations are readily obtained by considering equations (27) and (5) and the flow equations (14)-(15) and (29)-(30) and are the following:

$$L_{22} = (\rho/\rho_1)^2 \cdot a_{22} \quad (a), \quad L_{qq} = a_{qq} \quad (b) \quad (33)$$

$$L_{2q} = (\rho/\rho_1) \cdot a_{2q} = (\rho/\rho_1) \cdot a_{q2} = L_{q2} \quad (c)$$

Taking equations (33) into account it is at once concluded from Table 1 that the empirical coefficients corresponding to processes driven by forces such as $\text{grad } T$ and $\text{grad } x_2$, which are not involved in the mechanical force balance, are identical for both type of systems. These processes are diffusion, thermo diffusion, the Dufour effect and thermal conduction. On the other hand, the coefficients of processes such as pressure diffusion, sedimentation and the pressure and sedimentation thermal effects, due to forces included in the mechanical equilibrium ($\text{grad } P, (g + \Omega^2 \cdot r)$), are different in both types of system. Thus:

$$D = D' \quad D_T = D_T' \quad \lambda_c = \lambda_c' \quad \lambda_o = \lambda_o' \quad (34)$$

$$D_P \neq D_P' \quad s_2 \neq s_2' \quad \lambda_P \neq \lambda_P' \quad \lambda_s \neq \lambda_s' \quad (35)$$

In consequence the prime of the coefficients of eqs.(34) can be dropped from now on.

On the other hand, the inequalities of (35) correspond to the following relations:

$$D'_P/D_P = \lambda'_P/\lambda_P = V_2/(V_2 - M_2/\rho) \quad (36)$$

$$s'_2/s_2 = \lambda'_s/\lambda_s = M_2/(M_2 - \rho V_2) \quad (37)$$

While in the first relation (equation 36 and equations I-b', b, f', f) the factor M_2/ρ (displaced volume) is lacking in the expressions of the membrane coefficients D'_P and λ'_P , in the second relation (equation 37 and equations I-c', c, g', g) the factor $\rho \cdot V_2$ (displaced mass) is absent in the expressions of the membrane coefficients s'_2 and λ'_s . These factors represent buoyancy corrections. The *buoyancy effect* does not exist in membrane systems, as one component (the membrane substance) is immobile because of the mechanical constraint of the supporting frame. This conclusion has interesting consequences.

From equations (16) and (32) we know that the diagonal coefficients are always positive, while the off-diagonal coefficients may be positive or negative with an upper

value given by the last relations of (16) and (32). Accordingly we deduce from equations (I-a, h) and (34) that

$$D > 0, \lambda_o > 0 \quad (\text{membrane and fluid systems}) \quad (38)$$

and from equations (I-b', c') we derive that

$$D_p' > 0, \lambda_p' > 0 \quad (\text{membrane systems}) \quad (39)$$

Physically equation (39) has the following significance: in membrane systems the mobile component 2 migrates in the presence of a pressure gradient or a centrifugal field always toward the region of lower pressure and in the direction of the centrifugal field. On the other hand, the signs of the coefficients D_p and s_2 in fluid systems (equations I-b, c) depend on the signs of $(V_2 - M_2/\rho)$ and $(M_2 - \rho V_2)$, respectively. The difference $(M_2 - \rho V_2)$ may be written as [8]

$$M_2 - \rho V_2 = \left(\frac{\rho x_1}{M} \right) \cdot M_1 M_2 \cdot (\tilde{V}_1 - \tilde{V}_2), \quad (40)$$

as can easily be verified with (13) and

$$\bar{M} = x_1 M_1 + x_2 M_2, \quad \bar{V} = \bar{M} / \bar{\rho}, \quad c_i = x_i / \bar{V}, \quad \tilde{V}_i = V_i / M_i.$$

\bar{M} is the mean molar mass of the system, \bar{V} its molar volume and \tilde{V}_i the partial specific volume of component i . According to (40) and equations (I-b, c) in fluid systems the component of smaller partial specific volume migrates in the direction of the centrifugal field, but goes toward the higher pressure region in the presence of a pressure gradient, i.e.

$$\text{if } \tilde{V}_2 < \tilde{V}_1 \quad \text{then} \quad s_2 > 0, D_p < 0 \quad (\text{fluid systems}) \quad (41)$$

For gaseous mixtures, as $V_2 \approx V_1$, this behaviour corresponds to the component of greater molar mass [1].

A similar analysis with equivalent results corresponds to the pressure and sedimentation thermal effects, which are cross-events. From equations (I-f', g') we deduce that the coefficients λ_p' and λ_s' have always the sign of L_{q2} , i.e.

$$\text{if } L_{q2} > 0 \quad \text{then} \quad \lambda_p' > 0, \lambda_s' > 0 \quad (\text{membrane systems}) \quad (42)$$

and from equations (I-f, g) with (40) we obtain for λ_p and λ_s :

$$\text{if } \tilde{V}_2 < \tilde{V}_1, a_{q2} > 0 \quad \text{then} \quad \lambda_p < 0, \lambda_s > 0 \quad (\text{fluid systems}) \quad (43)$$

Furthermore, from equations (I-d, e), the ORR (equations 17 and 31) and (34) it follows that

$$\text{if } L_{2q} > 0 \quad \text{then} \quad D_T > 0, \lambda_c > 0 \quad (\text{fluid and membrane systems}) \quad (44)$$

According to equations (1) and (23) in the case of (44) the component 2 is enriched by thermo diffusion at the "cooler" region (fluid systems) [1] or at the "cooler" outer phase (membrane systems) [5], while heat flows by the Dufour effect (equations (2) and (24)) downwards the concentration gradient of component 2 in both types of systems. In the presence of a pressure gradient and/or a centrifugal field heat flows in this case ($L_{qq} > 0$) downwards the pressure gradient and in the direction of the centrifugal field in membrane systems (equation 42) and against the pressure gradient and in the direction of the centrifugal field in fluid systems (equations 43), if in these systems component 2 is the "denser" component.

Finally, the relations between empirical transport coefficients may be readily

obtained by combining the formulas of Table 1. The results are given in Table 2, where it is shown that there exist *ten* independent relations, *five* for each case, among these coefficients. *Four* are derived in a direct way and the *fifth* with consideration of the ORR. *Six* equations are known in the literature and the corresponding references are given in the table, while the other *four* relations are new.

Table 2: Relations between empirical transport coefficients

Fluid systems	Membrane systems
A) Without consideration of the ORR:	
From I-c and I-a: a) $\frac{s_2}{D} = \left(\frac{c_1 V_1}{x_1 \bar{V}} \right) \frac{M_2 - \rho V_2}{c_2 \mu_{22}^{(x)}}$ general expression [9, 10] of the Svedberg formula (1925 [11])	From I-c' and I-a': a') $\frac{s'_2}{D} = \left(\frac{c_1 V_1}{x_1 \bar{V}} \right) \frac{M_2}{c_2 \mu_{22}^{(x)}}$
From I-b and I-a: b) $\frac{D_P}{P.D} = \frac{V_2 - M_2 / \rho}{\mu_{22}^{(x)}}$ (Haase, 1950 [12])	From I-b' and I-a': b') $\frac{D'_P}{P.D} = \frac{V_2}{\mu_{22}^{(x)}}$ (Haase-Timmermann, 1982 [4])
From I-f and I-e: c) $\frac{\lambda_p}{\lambda_c} = - \frac{V_2 - M_2 / \rho}{\mu_{22}^{(x)}}$ (Haase, 1950 [12])	From I-f' and I-e': c') $\frac{\lambda'_p}{\lambda_c} = - \frac{V_2}{\mu_{22}^{(x)}}$
From I-g and I-e: d) $\frac{\lambda_s}{\lambda_c} = - \frac{M_2 - \rho V_2}{\mu_{22}^{(x)}}$	From I-g' and I-e': d') $\frac{\lambda'_s}{\lambda_c} = - \frac{M_2}{\mu_{22}^{(x)}}$
B) With consideration of the ORR:	
From I-e and I-d: e) $\frac{D_T}{T \lambda_c} = \frac{x_1 \bar{V}}{T \mu_{22}^{(x)}}$ (Haase, 1950 [12])	From I-e' and I-d': e') $\frac{D_T}{T \lambda_c} = \frac{x_1 \bar{V}}{T \mu_{22}^{(x)}}$ (Haase, 1966 [5])

Both sets of formulas of Table 2 correspond to continuous systems and the differences are due to the absence of the buoyancy effect in the membrane systems. So the well-known Svedberg equation (II-a) takes for membranes the different new form II-a'. On the other hand, equations (II-b', c') were already obtained by Haase [5] by means of a restricting assumption, which is unnecessary, as it has been shown elsewhere [4]. Both equation (II-b') and equation (II-c') are perfectly general for the interior of a

membrane. This is also true for equation (II-d’), which with its analogue for fluid systems, equation (II-d), are new relations, as well as the coefficients λ_s' and λ_s , which are introduced by the present paper. Furthermore, equations (II-e) and (II-e’) (see equation (34)) are identical as thermo-diffusion and the Dufour effect are not affected by the buoyancy effect.

Table 1 and 2 show that two mass transport coefficients are sufficient to describe all the transport processes, besides the thermal conductivity λ_o . It is quite reasonable and convenient to take as independent empirical transport coefficients the diffusion coefficient D , the thermo diffusion coefficient D_T (or the Dufour coefficient λ_c) and the thermal conductivity, as these coefficients are not affected by the buoyancy effect. In terms of these coefficients the relations of Table 2 can be summarised in the following schemes:

$$\frac{D}{c_2 \mu_{22}^{(x)}} = \begin{cases} = \frac{D_p / P}{c_2 (V_2 - M_2 / \rho)} = \frac{s_2 (\bar{V}^2 / V_1)}{(M_2 - \rho V_2)} \\ \text{(fluid systems)} \\ = \frac{D'_p / P}{c_2 V_2} = \frac{s'_2 (\bar{V}^2 / V_1)}{M_2} \\ \text{(membrane systems)} \end{cases} \quad (45)$$

and

$$-\frac{D_T}{x_1 \bar{V}} \stackrel{\text{(ORR)}}{=} \frac{\lambda_c}{\mu_{22}^{(x)}} = \begin{cases} = \frac{\lambda_p}{V_2 - M_2 / \rho} = \frac{\lambda_s}{M_2 - \rho V_2} \\ \text{(fluid systems)} \\ = \frac{\lambda'_p}{V_2} = \frac{\lambda'_s}{M_2} \\ \text{(membrane systems)} \end{cases} \quad (46)$$

Thus the knowledge of D and D_T (or λ_c) allows calculating, with the help of Irreversible Thermodynamics, all the other transport quantities. Moreover, some thermodynamic properties of the systems such as V_2 and $\mu_{22}^{(x)}$ must be measured independently. In the case of membranes, $\mu_{22}^{(x)}$ may be obtained from the sorption isotherm of the permeant.

An interesting alternative for the physical interpretation of the coefficients of heat transport induced by a mass flux may be obtained with the introduction of the quantity *Q_2 , the (internal) heat of transport of component 2, which is defined by [14, 5]:

$$^*Q_2 \equiv L_{2q} / L_{22} \stackrel{\text{(ORR)}}{=} \left[J_q / J_2 \right]_{x_q=0} \quad (47)$$

This definition holds for both types of systems, but it should be noted that in membranes a differentiation between “external” and “internal” heat of transport must be made [5]. The second expression of (47), derived with equations (i4-15), (29-30) and (33) and the ORR, allows to recognise immediately the physical significance of *Q_2 . In terms of *Q_2 and using the expressions of Table 1 the relations between the empirical transport

coefficients are:

$$\frac{^*Q_2}{x_1 \bar{V}} = -\frac{\mu_{22}^{(x)} \cdot D_T}{x_1 \bar{V} \cdot D} \stackrel{(ORR)}{=} -\frac{\lambda_o}{D} = \left\{ \begin{array}{l} = \frac{\mu_{22}^{(x)} \cdot \lambda_p}{(V_2 - M_2 / \rho) \cdot D} = \frac{\mu_{22}^{(x)} \cdot \lambda_2}{(M_2 - \rho V_2) \cdot D} \\ \text{(fluid systems)} \\ \\ = \frac{\mu_{22}^{(x)} \cdot \lambda'_p}{V_2 \cdot D} = \frac{\mu_{22}^{(x)} \cdot \lambda'_s}{M_2 \cdot D} \\ \text{(membrane systems)} \end{array} \right. \quad (48)$$

and

$$\frac{^*Q_2}{x_1 \bar{V}} \stackrel{(ORR)}{=} \left\{ \begin{array}{l} = \lambda_p \cdot P / D_p = (V_1 / \bar{V}) \cdot \lambda_s / s_2 \\ \text{(fluid systems)} \\ \\ = \lambda'_p \cdot P / D'_p = (V_1 / \bar{V}) \cdot \lambda'_s / s'_2 \\ \text{(membrane systems)} \end{array} \right. \quad (49)$$

where equations (49) are particularly simple and clear.

As has been mentioned in the preceding paragraph, there exist “external” and “internal” transport quantities in membrane systems [5]. “Internal” membrane coefficients are those discussed in this paper (equations 23-24; Table 1) and “external” coefficients are such as the mechanical (“hydraulic”) and the thermomechanical (thermoosmotic) permeabilities, the mechanocaloric (osmotic thermal) coefficient and the external thermal conductivity [5, 15]. The external quantities corresponding to the gravitational or centrifugal effect have not been defined so far in the literature.

The external quantities can be interpreted in terms of the internal coefficients. In particular permeation is related to diffusion and pressure diffusion inside the membrane [5] and by equation (II-b’) to diffusion alone [4]. By equation (II-a’) the permeability A_2 of component 2 may be related also to the membrane sedimentation coefficient s'_2 . Thus we have:

$$A_2 \equiv \frac{^*J_2}{\Delta P} \Big|_{\Delta \bar{x}_2=0, \Delta T=0} = \frac{V_2^*}{x_1 \bar{V}} \frac{D}{\mu_{22}^{(x)}} = \frac{c_2 V_2^*}{c_1 V_1} \frac{s'_2}{M_2}, \quad (50)$$

where the first expression has been obtained in Ref.[4] and the second one is derived by insertion of equation (II-e’) in the former. V_2^* is the molar volume of the permeant 2 in the pure phases outside the membrane [4]. The first relation, which is the general formula connecting permeability and diffusion, has been discussed already elsewhere [16] and satisfactorily tested by comparing direct measured values of permeabilities of artificial membranes with values calculated using diffusion and sedimentation data of concentrated polymer solutions [17, 18]. On the other hand, no experimental data of s'_2 are available, so far the author is aware, to test the second expression. As an extreme example, this expression describes the action of forcing out the water contained in a porous plug or a swollen sponge by a sudden quick shaking. In general this water flux can be described by the following formula:

$$J_2 = q_1 J_2 = q \cdot A_2^{(c)} \cdot X_c \quad (51)$$

where J_2 represents the total flow through the cross section q of the membrane, $A_2^{(c)}$ a centrifugal permeability and X_c a general centrifugal force, which is equal to $(g + \Omega^2 \cdot r)$ in the sedimentation experiments with $r \gg \delta$, where δ is the thickness of the membrane. By comparing (51) with the last term of equation (23) we obtain:

$$A_2^{(c)} = c_2 s_2' / c_1 V_1 \quad (52)$$

From (50) and (52) the relation between A_2 and $A_2^{(c)}$ follows immediately:

$$A_2 / V_2^* = A_2^{(c)} / M_2 \quad (53)$$

Thus, experimental measurements of s_2' in combination with equations (52)-(53) provide an interesting alternative for the determination of membrane permeability.

Conclusions

The foregoing analysis has shown the differences between transport quantities in membrane and fluid systems. These consist in the absence of the buoyancy effect in membrane systems. These systems are always in mechanical equilibrium and it is a characteristic that an additional force, the mechanical reaction of the supporting frame, is to be taken into account to guarantee this equilibrium. Now, as already stated at the end of Section 3, it is not necessary to describe this force with further details as it does not appear explicitly in the flow equations. This fact raises the question of whether the formulas obtained for membrane systems are restricted only to plane membranes supported by an external frame or if they are completely general and valid for any type of membrane systems, including systems such as vesicles or red blood cells, par example. In these cases no rigid support exists which compensates the unbalanced stresses of the membrane substance and a final "globular" configuration is found, which also represents a mechanical equilibrium situation. The tensions existing in different directions in the now curved membrane network are reduced in such a situation to a minimum with a finite resultant perpendicular to the surfaces which compensates the external force difference between both sides of the membrane and maintains mechanical balance within the membrane. This final tension in the network strands, the nature of which is viscoelastic, is now representative of F_1 in equation (22) and it must also not be described with further details [19]. Thus, our transport description also applies to these membranes and the answer to the question raised above is affirmative in the sense that our membrane formulas are completely general and valid for any type of membrane systems.

In following papers we will consider: (a) The extension of the foregoing description to ternary systems, which for membrane systems corresponds to the usual case of two permeants, the solvent and a solute. This case, normally described in terms of friction coefficients, will now be treated in terms of mobility coefficients as well as in terms of internal empirical transport coefficients. (b) A detailed analysis of the general permeability formula [4, 16] (first expression of equation (50)), where the effect of $\mu_{22}^{(x)}$ is very important. This permeability formula is only well known at the limit $c_2 \rightarrow 0$ (ideal dilute solution, Henry region). Under these conditions, $x_2 \mu_{22}^{(x)} \rightarrow RT$ and taking into account that $c_2 = x_2/V$ equation (50) takes the following, already classical, limiting forms:

$$\lim_{\substack{c_2 \rightarrow 0 \\ x_1 \rightarrow 1}} A_2 = A_2^\circ = c_2 V_2^\bullet \cdot D^\circ / RT \quad \left\{ \begin{array}{l} \text{a) permeation of pure gases:} \\ \quad V_2^\bullet = RT/P \\ \quad \rightarrow A_2^\circ = k_2^H \cdot D^\circ \\ \text{b) permeation of pure liquids:} \\ \quad V_2^\bullet = c_2 / c_2^\bullet \\ \quad \rightarrow A_2^\circ = k_2 \cdot D^\circ / RT \end{array} \right. \quad (54)$$

where $k_2^H (=c_2/P)$ is the Henry constant and $k_2 (=c_2/c_2^\bullet)$ is a partition constant. The index ($^\circ$) indicates limiting values.

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- [19] A practical example is the "tennis ball saver" device, by which the pressure of the balls is restored by putting them in a closed tube with compressed air. The mechanism may be more physical (by microporosity) than diffusional, but the basic principles are the same.