

# On the Validity of Onsager's Reciprocal Relations: I. Multi-component Isothermal Diffusion

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*Abstract:* - In this work is given an alternative proof of the Onsager's Reciprocal Relations for multi-component isothermal diffusion in the presence of external forces. The main characteristic of this proof is its simplicity. Moreover, this proof does not rely neither on the principle of microscopic reversibility nor on any particular statistical law as previous work.

*Key-Words:* Multi-component Diffusion, Friction Coefficients, Onsager's Reciprocal Relations (ORR)

## 1. Introduction

The field of irreversible thermodynamics provides us with a general framework for the macroscopic description of processes. It can be viewed as a branch of microscopic physics with applications to fluid mechanics, electromagnetic theory etc. The main issue of the thermodynamics of irreversible process is that can be viewed from the start as continuum theory, treating the state parameters of the theory as field variables i.e. continuous functions of space coordinates and time [1]-[3].

In the last century, irreversible thermodynamics was developed as a powerful theoretical tool for understanding the fundamental laws of many physical phenomena and industrial processes including transport phenomena, material manufacture, etc [4]-[9].

Irreversible thermodynamics is based on four postulates above and beyond those of equilibrium thermodynamics [1]-[3]:

1. The equilibrium thermodynamic relations apply to systems that are not in equilibrium, provided that the gradients are not too large (quasi-equilibrium postulate)

2. All the fluxes ( $j_i$ ) in the system may be written as linear relations involving all the thermodynamic

forces,  $X_i$ . (linearity postulate,  $j_i = \sum_{k=1}^n \Omega_{ik} X_k$  ;  
i=1,2,...n)

3. No coupling of fluxes and forces occurs if the difference in tensorial order of the flux and force is an odd number (Curie's postulate)

4. In the absence of magnetic fields and assuming linearly independent fluxes or thermodynamic forces the matrix of coefficients in the flux-force relations is symmetric. This postulate is known as the Onsager's Reciprocal Relations (ORR):  $\Omega_{ik} = \Omega_{ki}$ . Onsager derived these relations for the first time in 1931 [10]-[11]. He used the principle of microscopic reversibility by applying the invariance of the equations of motion for the atoms and molecules with respect to time reversal (the transformation  $t \rightarrow -t$ ). This means that the mechanical equations of motion (classical as well as quantum mechanical) of the particles are symmetric with respect to the time. In other words, the particles retrace their former paths if all velocities are reversed. Onsager also made a principal decision: the transition from molecular reversibility to microscopic reversibility can be made. It is important to remark that Onsager did not use a particular molecular model. As a consequence the results and limitations of the theory are valid for all materials, so that the theory can be related to continuum theory [12]. Casimir developed further this theory [13].

In the literature, there appear to be two groups of derivations of Onsager's reciprocal relations. In the first of these, it is assumed that the macroscopic laws of motion hold for the averages of the macroscopic coordinates (such as temperature

gradient, concentration gradient, etc) even if their values are microscopic. The second group assumes a definite statistical law for the path representing the system in phase space [14].

Although there is experimental evidence for the validity of ORR [15]-[17] doubts have been raised in the literature [18]; Moreover, the theoretical basis of ORR requires careful considerations as it was noticed by Prigogine and Kondepudi [19] in a recent review. The aim of this work is to eliminate any doubt about this principle by giving a simple proof for the isothermal multi-component diffusion which is important in many industrial processes [3], [20]-[23].

## 2. Problem Formulation

The uncompensated heat produced by an irreversible process is given by the dissipation function. The dissipation function is derived from an entropy balance [1]-[3]. The starting point of this work is the definition of the dissipation function  $\Psi$  in the absence of viscous flows for a non-elastic, non-reacting, isothermal & isotropic fluid containing n diffusing species [1]-[3],[12]:

$$\Psi = T\sigma = \sum_{i=1}^n j_i x_i ; i = 1,2,\dots,n \quad (1)$$

where  $\sigma$  is the rate of production of entropy per unit volume,  $T$  stands for the thermodynamic temperature and the molar flux  $j_i$  is measured relative to the velocity  $v$  of the centre of mass :

$$j_i = c_i(v_i - v) ; v = \sum_{i=1}^n M_i c_i v_i / \rho \quad (2)$$

$c_i$  is the molar concentration,  $M_i$  stands for the molar mass of the i-th species and the density  $\rho$  is given as:

$$\rho = \sum_{i=1}^n M_i c_i \quad (3)$$

The thermodynamic forces  $x_i$  are given as

$$x_i = -(\text{grad} \mu_i)_T + F_i \quad (4)$$

where

$$(\text{grad} \mu_i)_T = (\text{grad} \mu_i)_{T,p} + V_i \text{grad}(p) \quad (5)$$

is the gradient of i-th substance molar chemical potential,  $V_i$  stands for the partial molar volume of the i-th substance,  $p$  is the hydrostatic pressure and  $F_i$  represents the external force per mole of each substance. In this work, it is assumed that external forces act on the system or in other words there is no mechanical equilibrium.

At this point it is assumed that the quasi-equilibrium postulate holds true (see Introduction); Consequently, equilibrium thermodynamic relations such as the Gibbs-Duhem equation, can be applied to the system.

Schmitt and Graig [24] have shown that if the transformed thermodynamic forces

$$x'_i = x_i + M_i \left( \text{grad}(p) - \sum_{j=1}^n c_j F_j \right) / \rho \quad (6)$$

are used in the dissipation function, then

$$\sum_{i=1}^n c_i x'_i = 0 \quad (7)$$

The above equation follows from Eq. (3)-(5) and (6) by using the Gibbs - Duhem equation:

$$\sum_{i=1}^n c_i (\text{grad} \mu_i)_T = \text{grad}(p) \quad (8)$$

It is also necessary to introduce new fluxes, defined relative to an arbitrary reference velocity  $v^\#$ :

$$j_i^\# = c_i(v_i - v^\#) ; v^\# = \sum_{i=1}^n w_i v_i ; \sum_{i=1}^n w_i = 1 \quad (9)$$

If these new fluxes are introduced in Eq. (1), then the dissipation function is invariant under the

transformation to the new set of fluxes as well as to the thermodynamic forces [25]:

$$\Psi = \sum_{i=1}^n j_i^{\neq} x_i \quad (10)$$

Please note, that the fluxes  $j_i^{\neq}$  are also linearly dependent, since from eq (9)

$$\sum_{i=1}^n w_i j_i^{\neq} / c_i = 0 \quad (11)$$

By using Eq (11) the dissipation function (Eq. 10) is written as:

$$\Psi = \sum_{i=1}^n j_i^{\neq} x_i = \sum_{i,j=1}^{n-1} (\delta_{ij} + w_i c_j / c_i w_n) j_i^{\neq} x_j$$

or

$$\Psi = \sum_{i,j}^{n-1} A_{ij} j_i^{\neq} x_j \quad (12)$$

where

$$A_{ij} = \delta_{ij} + w_i c_j / c_i w_n ; i,j = 1,2,..,n-1 \quad (13)$$

Eq (12) can be regarded as the sum of fluxes and transformed dynamic forces:

$$\Psi = \sum_{i=1}^{n-1} j_i^{\neq} \left( \sum_{j=1}^{n-1} A_{ij} x_j \right) \quad (14)$$

or, equally as well, as the sum of products of transformed fluxes and thermodynamic forces:

$$\Psi = \sum_{j=1}^{n-1} \left( \sum_{i=1}^{n-1} A_{ij} j_i^{\neq} \right) x_j \quad (15)$$

The main idea of irreversible thermodynamics is to derive from the dissipation function fundamental macroscopic laws [1]-[3]; For this purpose the

linearity postulate (see Introduction) is applied to the fluxes and driving forces as these appear in the dissipation function. In our case there are n-1 independent fluxes and driving forces (Eq. 14-15). Consequently, by using the linearity postulate (see Introduction) the following equations between fluxes and thermodynamic driving forces are derived:

$$j_i^{\neq} = \sum_{j,k=1}^{n-1} l_{ij}^{\neq} (A_{jk} x_k) = \sum_{j,k=1}^{n-1} (l_{ik}^{\neq} A_{kj}) x_j \quad (16)$$

or

$$x_i = \sum_{j,k=1}^{n-1} r_{ij}^{\neq} (A_{kj} j_k^{\neq}) = \sum_{j,k=1}^{n-1} (r_{ik}^{\neq} A_{jk}) j_j^{\neq} \quad (17)$$

The quantities  $l_{ij}^{\neq}$  are the mobility coefficients and  $r_{ij}^{\neq}$  are the friction coefficients for diffusion, respectively. Since the fluxes and the thermodynamic forces are linear independent (Eq. 15-16), the Onsager reciprocal relations (ORR) state that

$$l_{ij}^{\neq} = l_{ji}^{\neq} \text{ or } r_{ij}^{\neq} = r_{ji}^{\neq} ; i,j = 1,2,..,n-1 \quad (18)$$

In the following section an alternative proof of the ORR is given.

### 3. Problem Solution

The starting point of this analysis is the introduction of the mobility coefficients ( $L_{ij}^{\neq}$ ) and the friction coefficients ( $R_{ij}^{\neq}$ ) by using the linearity postulate [26]:

$$j_i^{\neq} = \sum_{j=1}^n L_{ij}^{\neq} x_j ; i = 1,2,...,n \quad (19)$$

$$x_i = \sum_{j=1}^n R_{ij}^{\neq} j_j^{\neq} ; i = 1,2,...,n \quad (20)$$

In the above equations it is assumed that the mobility coefficients and the friction coefficients

are different than these defined in Eq (16)-(17). By using Eq. (11) and eliminating  $j_n^\#$  from Eq. (20), the following equation is derived:

$$x'_i = \sum_{j=1}^{n-1} \left( R_{ij}^\# - w_j c_n R_{in}^\# / c_j w_n \right) j_j^\# ; i=1,2..n \quad (21)$$

From Eq. (7), (13) and (17) it follows that

$$x'_n = - \sum_{i,j=1}^n c_i \left\{ r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# \right\} j_j^\# / c_n \quad (22)$$

Comparison of Eq. (17) and (22) with (21) gives

$$R_{ij}^\# - w_j c_n R_{in}^\# / c_j w_n = r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# ; i,j = 1,2..n-1 \quad (23)$$

and

$$R_{nj}^\# - w_j c_n R_{nn}^\# / c_j w_n = - \sum_{i=1}^{n-1} c_i \left\{ r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# \right\} j_j^\# / c_n ; j=1,2...n-1 \quad (24)$$

Following Tirrell and Harris [27] the friction coefficients (see Eq. 20) are introduced into Eq (7)

$$\sum_{k=1}^n c_k x'_k = \sum_{k=1}^n c_k \sum_{i=1}^n R_{ki}^\# j_i^\# = \sum_{i=1}^n j_i^\# \sum_{k=1}^n R_{ki}^\# c_k = 0$$

or

$$\sum_{k=1}^n R_{ki}^\# c_k = 0 ; i=1,2 \dots n \quad (25)$$

The above equation holds true due to the fact that the fluxes are defined relative to an arbitrary velocity and in the most general case,  $\sum_{i=1}^n j_i^\# \neq 0$

By introducing Eq. (25) into Eq. (24) it follows that

$$\left( \sum_{i=1}^{n-1} R_{ij}^\# c_i - \sum_{i=1}^{n-1} c_i r_{ij}^\# \right) - \left( w_j / c_j w_n \right) \left( R_{nn}^\# - \sum_{j=1}^{n-1} c_i c_j r_{ij}^\# / c_n^2 \right) = 0 ; j = 1,2..n-1 \quad (26)$$

As Eq. (26) holds for arbitrary concentrations, one could derive the following equations:

$$\sum_{i=1}^{n-1} c_i R_{ij}^\# = \sum_{i=1}^{n-1} c_i r_{ij}^\# ; j = 1,2 \dots n-1 \quad (27)$$

$$R_{nn}^\# = - \sum_{j=1}^{n-1} c_i c_j r_{ij}^\# / c_n^2 \quad (28)$$

From equation (27) it follows that

$$R_{ij}^\# = r_{ij}^\# ; i,j = 1,2...n-1 \quad (29)$$

The above equation could be viewed as a consequence of the Galilean invariance. Galilean transformations describe the change from one reference system into another by means of a uniform translation. In the classical theory, the physical laws and equations have to be invariant with respect to reference systems that are in relative translation at constant velocity. They are said to be invariant Galilean transformations [12]. In our case, the fluxes defined in Eq. (16)-(17) and in Eq. (19)-(20) could be viewed as fluxes defined with respect to different reference systems. According to Galilean transformation the physical laws and equations have to be invariant regarding the different system of reference. The mobility and the friction coefficients are physical quantities characterizing matter; Consequently, the mobility as well as the friction coefficients are independent of

the fluxes reference system and Eq. (29) hold true. In a similar way, the invariance of the dissipation function with respect to the flux reference velocity can be viewed as a consequence of the Galilean invariance.

By using Eq. (29) one can eliminate the first term of the left and the right hand-side of Eq (23) and the following equation is directly derived:

$$R_{in}^\# = - \sum_{j=1}^{n-1} c_j r_{ij}^\# / c_n ; i = 1, 2, \dots, n-1 \quad (30)$$

By multiplying the above equation by  $c_i/c_n$ , summing from  $i=1$  up to  $n-1$  and comparing the result with Eq. (28) the following equation is derived :

$$R_{in}^\# = - \sum_{j=1}^{n-1} c_j r_{ij}^\# / c_n ; i = 1, 2, \dots, n \quad (31)$$

By further using Eq. (29), the above equation is equivalently written as:

$$\sum_{j=1}^n c_j R_{ij}^\# = 0 ; i = 1, 2, \dots, n \quad (32)$$

By combining Eq. (25) and Eq. (33) it follows that

$$\sum_{j=1}^n c_j R_{ij}^\# = \sum_{j=1}^n c_j R_{ji}^\# = 0 ; i, j = 1, 2, \dots, n \quad (33)$$

or

$$R_{ij}^\# = R_{ji}^\# ; i, j = 1, 2, \dots, n \quad (34)$$

Given the above equality, by taking into account Eq. (29) the Onsager's reciprocal relations for the linearly independent friction coefficients are derived:

$$r_{ij}^\# = r_{ji}^\# ; i, j = 1, 2, \dots, n-1 \quad (35)$$

As the flux and the driving forces defined in Eq. (16)-(17) are linearly independent then the inverse matrix of the friction coefficients  $r_{ij}^\#$  exists; This inverse matrix is the matrix of mobility coefficients  $l_{ij}^\#$ . The matrix of friction coefficients is symmetrical (see Eq. 34) and also the inverse matrix, defined as the matrix of mobility coefficients has to be symmetrical [17]:

$$l_{ij}^\# = l_{ji}^\# ; i, j = 1, 2, \dots, n-1 \quad (35)$$

The above equations are the Onsager's Reciprocal Relations. The analysis presented in this work is not a new analysis; The idea of using Eq. (33) for proving ORR can be found in the pioneering work of Miller [17]. Moreover, the methodology for deriving Eq. (33) can be found in the work of Lorimer [25],[28] for the frame of reference for diffusion in membranes and liquids. However, Lorimer [25] used the equality between friction coefficients (Eq. 29) as an arbitrary assumption. In this work Eq. (29) was derived either as a consequence of the Galilean invariance or as a consequence of the relation between driving thermodynamic forces (see Eq. 7 and Eq. 25).

From a theoretical point of view this work shows that the ORR can be viewed as a consequence of the Galilean Invariance (GI). The GI causes the invariance of dissipation function as well as the friction coefficients invariance, regarding the reference system of fluxes. Moreover, it can be shown that in the presence of a magnetic field the Galilean invariance is replaced by the Lorentz transformations and in this case the Onsager's reciprocal relations have a different form [2].

#### 4. Conclusions

In the present work an alternative proof is given of the Onsager's reciprocal relations for multi-component isothermal diffusion in the presence of external forces (absence of mechanical equilibrium). This proof due to its simplicity eliminates any doubt about the ORR for isothermal diffusion. It is believed that this proof may be generalized to other processes than isothermal multi-component diffusion thus leading to a generalized framework for irreversible thermodynamics.

*References:*

- [1] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964.
- [2] S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, Dover Publications, New York, 1984
- [3] R.B. Bird, W.E. Stewart and E. N. Lightfoot, *Transport Phenomena*, John Wiley & Sons, New York, 2002
- [4] J.S. Vrentas, J.L. Duda and H.C. Ling, Enhancement of Impurity Removal from Polymer Films, *J. Appl. Pol. Sci.*, Vol. 30, 1985, pp.4499-4516.
- [5] C.F. Curtiss and R.B. Bird, Multicomponent Diffusion in Polymeric Liquids, *Proc. Nat. Acad. Sci. USA*, Vol. 93, 1996, pp. 7440-7445
- [6] P.E. Price, Jr and I.H. Romdhane, Multicomponent Diffusion Theory and Its Applications to Polymer-Solvent Systems, *AIChE J.*, Vol. 49, No. 2, 2003, pp. 309-322.
- [7] G.D. Verros and N.A. Malamataris, Multi-component Diffusion in Polymer Solutions, *Polymer*, Vol. 46, 2005, pp. 12626-12636
- [8] D. Matuszak and M. D. Donohue, Inversion of multicomponent diffusion equations, *Chem. Eng. Sci.*, Vol. 60, 2005, pp. 4359-4367.
- [9] P. J. A. M. Kerckhof and M. A. M. Geboers, Toward a Unified Theory of Isotropic Molecular Transport Phenomena, *AIChE J.*, Vol. 51, No. 1, 2005, pp. 79-121
- [10] L. Onsager, Reciprocal Relations in Irreversible Processes I, *Physical Review*, Vol. 37, 1931, pp. 405-426.
- [11] L. Onsager, Reciprocal Relations in Irreversible Processes II, *Physical Review*, Vol. 38, 1931, pp. 2265-2279.
- [12] G.D.C. Kuiken, *Thermodynamics of Irreversible Processes-Applications to Diffusion and Rheology*, John Wiley & Sons, New York, 1994
- [13] H.B.G. Casimir, On Onsager's Principle of Microscopic Reversibility, *Rev. Mod. Phys.*, Vol. 17, No. 2-3, 1945, pp. 343-350.
- [14] E.P. Wigner, Derivations of Onsager's Reciprocal Conditions, *J. Chem. Phys.*, Vol. 22, No. 54, 1954, pp. 1912-1915.
- [15] D.G. Miller, Thermodynamics of Irreversible Processes: the Experimental Verification of the Onsager Reciprocal Relations, *Chem. Rev.*, Vol. 60, No. 1, 1960 pp. 16-37.
- [16] D.G. Miller, Ternary Isothermal Diffusion and the Validity of the Onsager Reciprocity Relations, *J. Phys. Chem.*, Vol. 63, No. 8, 1959 pp. 570-578.
- [17] D.G. Miller, Application of Irreversible Thermodynamics to Electrolyte Solutions. I Determination of Ionic Transport Coefficients  $I_{ij}$  for Isothermal Vector Transport Processes in Binary Electrolyte Systems, *J. Phys. Chem.*, Vol. 70, No. 8, 1966, pp. 2639-2659.
- [18] B. D. Coleman and C. Truesdel, On the Reciprocal Relations of Onsager, *J. Chem. Phys.*, Vol. 33, No. 1, 1960, pp. 28-31.
- [19] D.P. Kondepudi and I. Prigogine, *Thermodynamics, Nonequilibrium*, in Encyclopedia of Applied Physics (Ed. G. L. Trigg), Wiley-VCH, 2003.
- [20] E.L. Cussler, *Multicomponent Diffusion*, Elsevier, Amsterdam, 1976
- [21] R. Taylor and R. Krishna, *Multicomponent Mass Transfer*. Wiley, New York, 1993.
- [22] E.L. Cussler, *Diffusion Mass Transfer in Fluid Systems*, Cambridge Univ. Press, Cambridge, 1997
- [23] J.C. Slattery, *Advanced Transport Phenomena*, Cambridge University Press, Cambridge, 1999
- [24] A. Schmitt and J.B. Craig, Frictional Coefficient Formalism and Mechanical Equilibrium in Membranes, *J. Phys. Chem.*, Vol. 81, No 13, 1977, pp. 1338- 1342.
- [25] J.W. Lorimer, Phenomenological Coefficients and Frames of Reference for Transport Processes in Liquids and Membranes Part I – Resistance Coefficients, Friction Coefficients and Generalized Diffusivities in Isothermal Systems *J. Chem. Soc. Faraday II*, Vol. 74, 1978, pp. 75-83.
- [26] L. Onsager, Theories and Problems of Liquid Diffusion, *Proc. Nat. Acad. Sci. USA*, Vol. 46, 1945, pp. 241-265.
- [27] H.J.V. Tyrrell and K.R. Harris, *Diffusion in Liquids A Theoretical and Experimental Study*, Butterworths, London, 1984
- [28] J.W. Lorimer, Phenomenological Coefficients and Frames of Reference for Transport Processes in Liquids and Membranes Part II – Resistance Coefficients in Non-Isothermal Systems *J. Chem. Soc. Faraday II*, Vol. 74, 1978, pp. 84-92.