

## On the Validity of Onsager Reciprocal Relations: II. Simultaneous Heat & Mass Transfer

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*Abstract:* - In this work an alternative proof of the Onsager Reciprocal Relations (ORR) for simultaneous heat & mass transfer in the presence of external forces is given. This proof is based on the transformation laws between fluxes defined relative to an arbitrary velocity (Galilean Invariance) thus eliminating any doubt about the ORR. It is believed that this proof may be generalized to other processes beyond multi-component diffusion and heat transfer thus leading to a generalized framework for transport phenomena and irreversible thermodynamics.

*Key-Words:* Multi-component Diffusion, Irreversible Thermodynamics, Onsager 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.

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,  $j_i = \sum_{k=1}^n \Omega_{ik} X_k$  ;  $i = 1, 2, \dots, n$ )

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 [4]-[5]. 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 [6]. Casimir developed further this theory [7].

In the literature, there appear to be two groups of derivations of Onsager 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 [8].

Although there is experimental evidence for the validity of ORR [9]-[11], doubts about this postulate have been raised in the literature [12]-[14]; For example, In *Rational Thermodynamics* [13] Truesdell remarks, "Onsager's and Casimir's claims that their assertions follow from *the principle of*

*microscopic reversibility* have been accepted with little question... the reversibility theorem and Poincare's recurrence theorem make irreversible behavior impossible for dynamical systems in a classical sense. Something must be added to the dynamics of conservative systems, something not consistent with it, in order to get irreversibility at all." [14] Moreover, it is believed that if equilibrium relations such as the Gibbs-Duhem equations are added in the mathematical model for multi-component diffusion by simply applying the quasi equilibrium postulate, then the ORR are not necessarily fulfilled; (ref 2, p. 67-69). Therefore the theoretical basis of ORR requires careful considerations as was also noticed by Prigogine and Kondepudi [15] in a recent review. In our previous work [16] a simple proof for the isothermal multi-component diffusion case was given. This proof was based on the transformation laws between fluxes defined relative to an arbitrary velocity (Galilean Invariance) The aim of this work is to investigate the theoretical basis of this principle by extending the previously described methodology to the simultaneous heat transfer and mass transfer which is important in many industrial processes [3], [17]-[26].

## 2. Derivation of the Onsager Reciprocal Relations

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, isotropic fluid containing n diffusing species [28]-[29]:

$$\Psi = T\sigma = \sum_{i=1}^n j_i^{\neq} x_i' + j_q' x_u ; x_u = -gradT / T ;$$

$$j_q' = j_q - \sum_{i=1}^n H_i j_i ; -\nabla \cdot j_q = \rho \frac{dq}{dt} ; i = 1, 2, \dots, n$$

(1)

where  $\sigma$  is the rate of production of entropy per unit volume,  $T$  stands for the thermodynamic temperature,  $H_i$  is the partial molar of species  $i$ ,  $q$  represents heat,  $\rho$  is the density. The molar flux  $j_i^{\neq}$  is measured relative to an arbitrary velocity  $v^{\neq}$  :

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

$$\rho = \sum_{i=1}^n M_i c_i$$

(2)

$c_i$  is the molar concentration,  $M_i$  stands for the molar mass of the  $i$ -th species. Please note, that the fluxes  $j_i$  are also linearly dependent, since from eq

$$(2): \sum_{i=1}^n w_i j_i^{\neq} / c_i = 0$$

(3)

The thermodynamic forces  $x_i'$  are given as [27]-[29]:

$$x_i' = -(grad \mu_i)_{T,P} + F_i' - V_i grad(p)$$

$$F_i' = F_i + M_i \left( grad(p) - \sum_{j=1}^n c_j F_j \right) / \rho$$

(4)

$grad \mu_i$  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. By using Eq (3) the dissipation function (Eq. 1) is written as:

$$\Psi = \sum_{i,j}^{n-1} A_{ij} j_i^{\neq} x_j' + j_q' x_u$$

$$A_{ij} = \delta_{ij} + w_i c_j / c_i w_n ; i, j = 1, 2, \dots, n-1$$

(5)

Eq (5) can be regarded as the sum of fluxes and transformed dynamic forces:

$$\Psi = \sum_{i=1}^{n-1} j_i^{\neq} \left( \sum_{j=1}^{n-1} A_{ij} x_j' \right) + j_q' x_u =$$

$$= \sum_{j=1}^{n-1} \left( \sum_{i=1}^{n-1} A_{ij} j_i^{\neq} \right) x_j' + j_q' x_u$$

(6)

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 [16]. Consequently, by using the linearity postulate (see Introduction) the following equations between

fluxes and thermodynamic driving forces are derived:

$$\begin{aligned}
 j_i^\# &= \sum_{j,k=1}^{n-1} l_{ij}^\# (A_{jk} x_k') + l_{iu}^\# x_u \\
 j_q^\# &= \sum_{j,k=1}^{n-1} l_{uj}^\# (A_{jk} x_k') + l_{uu}^\# x_u \\
 x_i' &= \sum_{j,k=1}^{n-1} r_{ij}^\# (A_{kj} j_k^\#) + r_{iu}^\# x_u \\
 x_u &= \sum_{j,k=1}^{n-1} r_{uj}^\# (A_{kj} j_k^\#) + r_{uu}^\# x_u \quad (7)
 \end{aligned}$$

The quantities  $l^\#$  are the conductivity coefficients and  $r^\#$  are the resistance coefficients for diffusion or heat transfer, respectively. Since the fluxes and the thermodynamic forces are linear independent (Eq. 7), the Onsager reciprocal relations (ORR) state that

$$\begin{aligned}
 l_{ij}^\# &= l_{ji}^\# , \quad l_{uj}^\# = l_{ju}^\# \quad \text{or} \\
 r_{ij}^\# &= r_{ji}^\# , \quad r_{uj}^\# = r_{ju}^\# \quad i,j = 1,2,\dots,n-1 \quad (8)
 \end{aligned}$$

The starting point of this analysis is the introduction of the resistance coefficients ( $R^\#$ ) by using the linearity postulate [2], [28]-[30]:

$$\begin{aligned}
 x_i' &= \sum_{j=1}^n R_{ij}^\# j_j^\# + R_{iu}^\# j_q \\
 x_u &= \sum_{j=1}^n R_{uj}^\# j_j^\# + R_{uu}^\# j_q \quad ; i = 1,2,\dots,n \quad (9)
 \end{aligned}$$

In the above equations it is assumed that the resistance coefficients are different than these defined in Eq (7). By using Eq. (3) and eliminating  $j_n^\#$  from Eq. (9), the following equation is derived:

$$\begin{aligned}
 x_i' &= \sum_{j=1}^{n-1} \left( R_{ij}^\# - w_j c_n R_{in}^\# / c_j w_n \right) j_j^\# + R_{iu}^\# j_q \\
 x_u &= \sum_{j=1}^{n-1} \left( R_{uj}^\# - w_j c_n R_{un}^\# / c_j w_n \right) j_j^\# + R_{uu}^\# j_q \\
 &\quad i=1,2,\dots,n \quad (10)
 \end{aligned}$$

But from the Gibbs-Duhem theorem the following

$$\text{equation holds[16]: } \sum_{i=1}^n c_i x_i' = 0 \quad (11)$$

From Eq. (5b), (7) and (11) it follows that

$$\begin{aligned}
 x_n' &= - \sum_{i,j=1}^n c_i \left\{ r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# \right\} j_j^\# / c_n \\
 &+ \sum_{i=1}^{n-1} c_i r_{iu}^\# / c_n \quad (12)
 \end{aligned}$$

Comparison of Eq. (7) and (12) with Eq. (10) gives:

$$\begin{aligned}
 R_{ij}^\# - w_j c_n R_{in}^\# / c_j w_n &= r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# \\
 R_{iu}^\# &= r_{iu}^\# \quad i,j = 1,2,\dots,n-1 \quad (13)
 \end{aligned}$$

$$\begin{aligned}
 R_{nj}^\# - w_j c_n R_{nn}^\# / c_j w_n &= \\
 = - \sum_{i=1}^{n-1} c_i \left\{ r_{ij}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{ik}^\# \right\} j_j^\# / c_n \quad (14)
 \end{aligned}$$

$$\sum_{i=1}^{n-1} c_i r_{iu}^\# + c_n R_{nu}^\# = 0 \quad \text{or by using (13b)}$$

$$\sum_{i=1}^n c_i R_{iu}^\# = 0 \quad (15)$$

$$\begin{aligned}
 R_{uj}^\# - w_j c_n R_{un}^\# / c_j w_n &= r_{uj}^\# + \left( w_j / c_j w_n \right) \sum_{k=1}^{n-1} c_k r_{uk}^\# \\
 R_{uu}^\# &= r_{uu}^\# \quad (16)
 \end{aligned}$$

By substituting Eq. (9) into Eq. (11) the following equation is derived [31]:

$$\sum_{i=1}^n c_i \sum_{j=1}^n R_{ij}^\# j_j^\# + \sum_{i=1}^n c_i R_{iu}^\# j_q = 0$$

From this equation and by taking into account that the total sum of molar fluxes relative to an arbitrary velocity, in the most general case, is not equal to

$$\text{zero it follows that } \sum_{i=1}^n c_i R_{ij}^\# = 0 \quad (17)$$

By introducing Eq. (17) into Eq. (14) it follows that

$$\begin{aligned}
 &\left( \sum_{i=1}^{n-1} R_{ij}^\# c_i - \sum_{i=1}^{n-1} c_i r_{ij}^\# \right) \\
 &- \left( w_j / c_j w_n \right) \left( R_{nn}^\# - \sum_{j=1}^{n-1} c_j r_{ij}^\# / c_n^2 \right) = 0 \\
 &j = 1,2,\dots,n-1 \quad (18)
 \end{aligned}$$

As Eq. (18) holds for arbitrary concentrations, one could derive the following equations:

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

$$R_{nn}^{\neq} = - \sum_{j=1}^{n-1} c_j r_{nj}^{\neq} / c_n^2 \quad (19)$$

From the above equation it follows that:

$$R_{ij}^{\neq} = r_{ij}^{\neq} \quad ; i,j = 1,2 \dots n-1 \quad (20)$$

By using Eq. (20) one can eliminate the first term of the left and the right hand-side of Eq (13) and the following equation is directly derived:

$$R_{in}^{\neq} = - \sum_{j=1}^{n-1} c_j r_{ij}^{\neq} / c_n \quad ; i = 1,2 \dots n-1 \quad \text{or}$$

$$\sum_{j=1}^n c_j R_{ij}^{\neq} = 0 \quad (21)$$

By using Eq. (17)-(21) it follows that

$$\sum_{j=1}^n c_j R_{ij}^{\neq} = \sum_{j=1}^n c_j R_{ji}^{\neq} = 0 \quad ; i, j = 1,2 \dots n \quad \text{or}$$

$$R_{ij}^{\neq} = R_{ji}^{\neq} \quad ; i, j = 1,2 \dots n \quad (22)$$

These are the Onsager reciprocal relations for the diffusion resistance coefficients.

At this point one has to resort to the Galilean invariance for the heat transfer resistance coefficients. The Galilean transformation describes 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.[6] In our case, the fluxes or the driving forces defined in Eq. (7) and in Eq. (19)-(20) could be viewed as quantities 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 resistance coefficients are physical quantities characterizing matter; Consequently, they are independent of the fluxes reference system and the following equation holds true:  $R_{ij}^{\neq} = r_{ij}^{\neq}$ . By substituting this equation into Eq. 16 and by taking into account Eq.(13b) and 15 it follows that

$$\sum_{i=1}^n c_i R_{iu}^{\neq} = \sum_{i=1}^n c_i R_{ui}^{\neq} = 0 \quad \text{or} \quad R_{ij}^{\neq} = R_{ju}^{\neq}.$$

Given this equality, by taking into account Eq. (13b) the

Onsager reciprocal relations for the  $r_{uj}^{\neq}$  are derived:

$r_{uj}^{\neq} = r_{ju}^{\neq} ; l_{uj}^{\neq} = l_{ju}^{\neq} \quad ; j=1,2 \dots n-1.$  It should be noted here that this work follows closely the work of Lorimer [27]-[28]. However, in this work the equality  $R_{ij}^{\neq} = r_{ij}^{\neq}$  is derived as a consequence of the Galilean transformation and the equality  $R_{ij}^{\neq} = r_{ij}^{\neq}$  (Eq. 20) is derived from the Gibbs-Duhem theorem.

### 3. Results & Conclusions

In the present work an alternative proof of the Onsager reciprocal relations (ORR) for simultaneous heat & mass transfer in the presence of external forces (absence of mechanical equilibrium) is given. This proof is based on the transformation laws between fluxes defined relative to an arbitrary velocity (Galilean Invariance, GI) eliminating thus any doubt about the ORR for the multi-component diffusion case. Moreover, it is shown that that if the Gibbs-Duhem equations are added in the mathematical model for the multi-component diffusion by simply applying the quasi equilibrium postulate, the ORR are also fulfilled.

It is also shown that every model for simultaneous heat & mass transfer should satisfy the Onsager reciprocal relations. It is believed that this proof may be generalized to other processes beyond simultaneous & heat mass transfer thus leading to a generalized framework for irreversible thermodynamics and transport phenomena.

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