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Second law analysis of combined heat and mass transfer phenomena

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Abstract—Expressions are derived for entropy generation due to heat and mass transfer processes in a multi-component fluid. These show that the entropy generation due to the coupling effect between heat and mass transfer has been calculated incorrectly in recent publications. This contribution is zero unless the thermal diffusion and diffusion-thermo effects are explicitly included in the theory. Restrictions on the applicability of expressions used recently for entropy generation due to mass transfer are identified. An ideal binary fluid is used to illustrate the analysis in the limit where the pressure gradient is small in the direction of the diffusion flux.

1. INTRODUCTION

THE LOSS due to processes irreversibility within individual system components is an important parameter in process system design [1]. This loss can be calculated using second law analysis, either from the rate of entropy generation within the relevant control volume, or from the unbalanced rate of input of exergy. The entropy approach is especially useful for the purpose of system optimization because the losses contributed by distinguishable sub-processes can be separately evaluated [1].

Much of the interest in second law optimization has focused on entropy generation due to heat transfer and fluid friction, and the trade-off between these irreversibilities, as design parameters are changed [2]. Recently this analysis has been extended to include mass transfer processes [3–7]. In particular San *et al.* [5, 6] investigated entropy generation in fluid flow in a two-dimensional channel, taking into account isothermal mass transfer as well as combined heat and mass transfer. The analysis of San *et al.* has been reviewed subsequently by Bejan [1, 8]. Poulikakos and Johnson [7] also examined entropy generation in combined heat and mass transfer.

The equations developed by San *et al.* [5, 6] are based on expressions for the rate of entropy generation per unit volume in a Newtonian fluid given by Hirschfelder *et al.* [9]. By considering the fluid to be a binary mixture of two ideal gases, San *et al.* obtained a simplified expression for the molar chemical potential of the components. The mass diffusion rate was assumed to be small and the analysis also invoked other approximations.

We note that San *et al.* [5, 6] and Bejan [1, 8], indicated that there is a significant entropy generation term involving products of the type $\nabla T \cdot \nabla c_k$. This term was attributed to the coupling between simultaneous heat and mass transfer processes. Here we show that this term is absent from the entropy generation equation, unless the analysis explicitly accounts for the thermal diffusion effect and diffusion-thermo effect. These effects were not included in the discussion in refs. [1, 5, 6, 8]. Moreover, when these effects are included, we find that the coupling term is typically very small compared to the terms obtained by San *et al.* [5, 6] and Bejan [1, 8]. In addition we consider expressions given by these authors for the rate of entropy generation due to mass transfer alone in a binary mixture. We show that expressions involving terms of the type $(\nabla c_A)^2$ are only applicable when the binary system is very dilute, the molar concentration is essentially uniform and the pressure gradient in the direction of the diffusion flux is negligible.

2. ENTROPY GENERATION

In a recent paper [10] we obtained a general exergy balance equation which is applicable to a fluid mixture subject to heat conduction, mass diffusion, fluid friction and chemical reactions. The equation relates the rate of entropy production per unit volume, σ, to the non-flow exergy function, $b_{T\mathrm{n}}$, the steady flow exergy function, $b_{T\mathrm{s}}$, and the steady flow exergy flux, $\mathbf{J}_{b\mathrm{s}}$

$$\frac{\partial}{\partial t}(\rho b_{T\mathrm{n}})+\nabla\cdot(\rho b_{T\mathrm{s}}\mathbf{v}+\mathbf{J}_{b\mathrm{s}}) = -T_{\mathrm{o}}\sigma. \qquad (1)$$

This equation, which is an example of the Gouy–Stodola theorem [2], provides a general link between the exergy formulation of second law analysis and the entropy generation method. The volumetric rate of entropy generation is expressed as the sum of four process contributions

$$\sigma = \mathbf{J}_q\cdot\nabla\left(\frac{1}{T}\right)+\sum_{k=1}^{K}\mathbf{J}_k\cdot\left\{\frac{\mathbf{F}_k}{T}-\nabla\left(\frac{\mu_k}{T}\right)\right\}$$
$$-\frac{1}{T}\mathbf{P}^{\mathrm{v}}:\nabla\mathbf{v}-\frac{1}{T}\sum_{j=1}^{R}J_j\left(\sum_{k=1}^{K}\nu_{kj}\mu_k\right). \qquad (2)$$

NOMENCLATURE

A, B	species label in binary mixture
b	specific exergy function [J kg^{-1}]
b_k	partial specific exergy function for species k [J kg^{-1}]
c_k	molar concentration for species k [mol m^{-3}]
D_{kj}, $\mathscr{D}_{km}$	diffusion coefficient [m^2 s^{-1}]
D', D''	thermal diffusion coefficient, Dufour coefficient [m^2 s^{-1} K^{-1}]
$\mathbf{F}$	external force per unit mass [N kg^{-1}]
h_k	partial specific enthalpy for species k [J kg^{-1}]
$\mathbf{J}_k$	mass flux for species k relative to barycentric velocity [kg m^{-2} s^{-1}]
$\bar{\mathbf{J}}_k$	molar flux for species k relative to barycentric velocity [mol m^{-2} s^{-1}]
$\bar{\mathbf{J}}_k^*$	molar flux for species k relative to molar average velocity [mol m^{-2} s^{-1}]
$\mathbf{J}_q$	internal energy (heat) flux [J m^{-2} s^{-1}]
$\mathbf{J}'_q$	heat flux, excluding enthalpy diffusion currents [J m^{-2} s^{-1}]
J_j	rate per unit volume for the jth chemical reaction [kg s^{-1} m^{-3}]
k	thermal conductivity [J m^{-1} s^{-1} K^{-1}]
K	number of components in mixture
M_k	molecular weight of species k [kg mol^{-1}]
P	thermodynamic pressure [N m^{-2}]
$\mathbf{P}^{\mathrm{v}}$	viscous part of pressure tensor [N m^{-2}]
R	number of chemical reactions in mixture
$\bar{R}$	molar gas constant [J mol^{-1} K^{-1}]
s	specific entropy [J kg^{-1} K^{-1}]
s_k	partial specific entropy of species k [J kg^{-1} K^{-1}]
$\bar{s}_k$	partial molar entropy of species k [J mol^{-1} K^{-1}]
t	time [s]
T	temperature [K]
v_k	partial specific volume of species k [m^3 kg^{-1}]
$\bar{v}_k$	partial molar volume of species k [m^3 kg^{-1}]
$\mathbf{v}$	barycentric (mass average) velocity of mixture [m s^{-1}]
$\mathbf{v}^*$	molar average velocity of mixture [m s^{-1}]
$\mathbf{v}_k$	velocity for species k [m s^{-1}]
x_k	mole fraction for species k in the mixture.

Greek symbols

μ_k	specific chemical potential for species k [J kg^{-1}]
$\bar{\mu}_k$	molar chemical potential for species k [J mol^{-1}]
ν_{kj}	specific stoichiometric coefficient for species k in reaction j
ρ	mass density for mixture [kg m^{-3}]
ρ_k	mass concentration of species k [kg m^{-3}]
σ	rate of entropy generation per unit volume [J K^{-1} s^{-1} m^{-3}]
ω	mass fraction.

Subscripts

d	diffusion
j	jth chemical reaction
k	kth species of mixture
n	non-flow
o	value at the environmental dead state
q	heat transfer
s	steady flow
T	derivative at constant temperature
Tn, Ts	total non-flow, total steady flow.

The terms on the right-hand side represent, respectively, the irreversibilities due to heat transfer, mass transfer, viscous flow and chemical reactions [10–12]. In this paper we restrict our attention to the first two terms only and we assume also that external body forces, $\mathbf{F}_k$, can be neglected. Thus, denoting the heat and mass transfer terms by σ_{qd}, and setting $\mathbf{F}_k = 0$, we have

$$\sigma_{qd} = \mathbf{J}_q \cdot \nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{K} \mathbf{J}_k \cdot \nabla\left(\frac{\mu_k}{T}\right). \tag{3}$$

Now the energy flux, $\mathbf{J}_q$, is the sum of the heat flux, $\mathbf{J}'_q$, and the enthalpy flux due to diffusion

$$\mathbf{J}_q = \mathbf{J}'_q + \sum_{k=1}^{K} \mathbf{J}_k h_k \tag{4}$$

where h_k is the partial specific enthalpy [10–12]. Substituting this expression in equation (3), we may express the heat and mass transfer terms as follows:

$$\sigma_{qd} = \sigma'_q + \sigma'_d \tag{5}$$

where

$$\sigma'_q = \mathbf{J}'_q \cdot \nabla\left(\frac{1}{T}\right) \tag{6}$$

and

$$\sigma'_d = -\frac{1}{T}\sum_{k=1}^{K} \{(\mathbf{J}_k s_k)\nabla T + \mathbf{J}_k \cdot \nabla\mu_k\}. \tag{7}$$

Here s_k is the partial specific entropy and we have used the relation, $\mu_k = h_k - Ts_k$.

For comparative purposes, it is useful to transform from the mass flux, $\mathbf{J}_k$, and the partial specific quantities, s_k, h_k, μ_k, to the corresponding molar flux and partial molar quantities. The equation of Hirschfelder *et al.* [9], which is utilized in refs. [1, 5, 6], is expressed in these terms. For later reference we define density $$\rho = \sum_{k=1}^{K} \rho_k \quad (8)$$

mass fraction $$\omega_k = \rho_k/\rho \quad (9)$$

barycentric velocity $$\mathbf{v} = \sum_{k=1}^{K} \omega_k \mathbf{v}_k \quad (10)$$

molar concentration $$c_k = \rho_k/M_k. \quad (11)$$

Then the partial molar entropy, molar chemical potential and the molar diffusion flux are, respectively

$$\bar{s}_k = M_k s_k \quad (12)$$

$$\bar{\mu}_k = M_k \mu_k \quad (13)$$

$$\bar{\mathbf{J}}_k = \frac{1}{M_k}\mathbf{J}_k = c_k(\mathbf{v}_k - \mathbf{v}). \quad (14)$$

Substituting into equation (7), we obtain the rate of entropy generation per unit volume, due to diffusion

$$\sigma'_\mathrm{d} = -\frac{1}{T}\sum_{k=1}^{K} \{(\bar{\mathbf{J}}_k \bar{s}_k)\cdot\nabla T + \bar{\mathbf{J}}_k \cdot \nabla\bar{\mu}_k\}. \quad (15)$$

We note that the molar diffusion flux $\bar{\mathbf{J}}_k$ is measured relative to the barycentric, or mass average, velocity [11–14]. However, under certain conditions the barycentric velocity in equation (15) may be replaced by an arbitrary velocity. These requirements follow from a theorem due to Prigogine [15].

3. PRIGOGINE THEOREM

The Prigogine theorem, which is summarized by De Groot and Mazur [11], follows from the Gibbs–Duhem relation for a multi-component system. This latter relation can be expressed in terms of partial molar quantities as

$$\sum_{k=1}^{K} c_k\{\bar{s}_k\nabla T + \nabla\bar{\mu}_k\} = \nabla P. \quad (16)$$

Hence under the condition of mechanical equilibrium, when $\nabla P = 0$ and $\mathbf{F}_k = 0$, equation (15) can be rewritten as

$$\sigma'_\mathrm{d} = -\frac{1}{T}\sum_{k=1}^{K} c_k(\mathbf{v}_k - \mathbf{v}_\mathrm{a})\cdot(\bar{s}_k\nabla T + \nabla\bar{\mu}_k) \quad (17)$$

where $\mathbf{v}_\mathrm{a}$ is an arbitrary velocity. In this situation we may therefore use $\bar{\mathbf{J}}_k^*$, instead of $\bar{\mathbf{J}}_k$, in equation (15). Here $\bar{\mathbf{J}}_k^*$ is the molar diffusion flux measured relative to the molar average velocity, $\mathbf{v}^*$

$$\bar{\mathbf{J}}_k^* = c_k(\mathbf{v}_k - \mathbf{v}^*) \quad (18)$$

where the molar average velocity is

$$\mathbf{v}^* = \sum_{k=1}^{K} x_k \mathbf{v}_k \quad (19)$$

the mole fraction, x_k, is defined as

$$x_k = c_k/c \quad (20)$$

and c, the total molar concentration, is

$$c = \sum_{k=1}^{K} c_k. \quad (21)$$

Then, under the condition that ∇P can be neglected, equation (15) may be expressed as

$$\sigma'_\mathrm{d} = -\frac{1}{T}\sum_{k=1}^{K} \{(\bar{\mathbf{J}}_k^* \bar{s}_k)\nabla T + \bar{\mathbf{J}}_k^* \nabla\bar{\mu}_k\}. \quad (22)$$

We note that equation (2) together with equations (7) and (15) correspond to the expression for the volumetric rate of entropy production used by San *et al.* [5, 6], and also by Bejan [1, 8]. Equation (22) is also of the same form. The term $\mu/T\Phi$ in equation (115) of Bejan [1] corresponds to $(-1/T)\mathbf{P}^\mathrm{v} : \nabla\mathbf{v}$ which represent viscous dissipation in equation (2). In addition we note the following equations for the sum of the mass fluxes which are useful in applying equations (7), (15) and (22):

$$\sum_{k=1}^{K} \mathbf{J}_k = 0 \quad (23)$$

$$\sum_{k=1}^{K} \bar{\mathbf{J}}_k = c(\mathbf{v}^* - \mathbf{v}) \quad (24)$$

$$\sum_{k=1}^{K} \bar{\mathbf{J}}_k^* = 0. \quad (25)$$

These relations show that only $K-1$ of the K diffusion fluxes are independent. Hence we cannot say that only one species in a system diffuses when we use the concept of mass diffusion fluxes relative to some average velocity.

4. DERIVATIVE EXPRESSIONS

The natural thermodynamic variables for the chemical potential (partial specific Gibbs function), μ_k, are T, P and the $K-1$ independent mass fractions ω_i of the K species; for $\bar{\mu}_k$ the natural variables are T, P and the independent mole fractions, x_i. Thus the gradients of μ_k and $\bar{\mu}_k$ are [16]

$$\nabla\mu_k = -s_k\nabla T + v_k\nabla P + \sum_{i=1\ i\neq k}^{K} \mu_{ki}^{\omega}\nabla\omega_i \quad (26)$$

or

$$\nabla\bar{\mu}_k = -\bar{s}_k\nabla T + \bar{v}_k\nabla P + \sum_{i=1\ i\neq k}^{K} \bar{\mu}_{ki}^{x}\nabla x_i \quad (27)$$

where the partial specific quantities are related to the derivatives of the chemical potential by

$$s_k = -\left(\frac{\partial\mu_k}{\partial T}\right)_{P,\omega_s} \quad (28)$$

$$v_k = \left(\frac{\partial\mu_k}{\partial P}\right)_{T,\omega_s} \quad (29)$$

and

$$\mu_{ki}^{\omega} = \left(\frac{\partial\mu_k}{\partial\omega_i}\right)_{T,P,\omega_s,s\neq i,k} \quad (30)$$

Similar relations apply to the partial molar derivatives and substituting these into equations (7) and (15) yields

$$\sigma'_{\mathrm{d}} = -\frac{1}{T}\sum_{k=1}^{K} \mathbf{J}_k \cdot \left\{ v_k \nabla P + \sum_{i=1\ i\neq k}^{K} \mu^{\omega}_{ki} \nabla \omega_i \right\} \qquad (31)$$

$$= -\frac{1}{T}\sum_{k=1}^{K} \bar{\mathbf{J}}_k \cdot \left\{ \bar{v}_k \nabla P + \sum_{i=1\ i\neq k}^{K} \bar{\mu}^{x}_{ki} \nabla x_i \right\}. \qquad (32)$$

We see that the term involving products of mass fluxes and the temperature gradient in equations (7), (15) and (22) has cancelled out with the corresponding products arising in $\nabla\mu_k$ and $\nabla\bar{\mu}_k$. Thus the temperature gradient mass flux products in these equations vanish and they do not represent any contribution to the entropy generation. This result disagrees with the interpretation given in refs. [1, 5, 6, 8] in which the product term is attributed to a coupling effect between mass diffusion and heat flow.

The absence of the temperature gradient in the thermodynamic force term corresponding to the flux terms $\mathbf{J}_k$ and $\bar{\mathbf{J}}_k$ in equations (31) and (32) can be seen explicitly by considering the gradient of the chemical potential evaluated at constant temperature. From equation (26)

$$(\nabla\mu_k)_T = v_k \nabla P + \sum_{i=1\ i\neq k}^{K} \mu^{\omega}_{ki} \nabla \omega_i \qquad (33)$$

and hence, equation (31) becomes

$$\sigma'_{\mathrm{d}} = -\frac{1}{T}\sum_{k=1}^{K} \mathbf{J}_k \cdot (\nabla\mu_k)_T. \qquad (34)$$

A similar form applies to the molar quantities, $\bar{\mathbf{J}}_k$ and $\bar{\mu}_k$. Furthermore, under conditions of mechanical equilibrium, we see from the Prigogine theorem that we may use $\bar{\mathbf{J}}^*_k$ instead of $\bar{\mathbf{J}}_k$ in equation (32). Since under this assumption we set $\nabla P = 0$, we obtain the required results

$$\sigma'_{\mathrm{d}} = -\frac{1}{T}\sum_{k=1}^{K} \bar{\mathbf{J}}^*_k \cdot (\nabla\bar{\mu}_k)_{T,P} \qquad (35)$$

$$= -\frac{1}{T}\sum_{k=1}^{K} \bar{\mathbf{J}}^*_k \left\{ \sum_{i=1\ i\neq k}^{K} \bar{\mu}^{x}_{ki} \nabla x_i \right\}. \qquad (36)$$

5. FOURIER AND FICK LAWS

For mixtures, the heat flux $\mathbf{J}'_q$ consists of the conductive heat flux $\mathbf{J}^{(c)}_q$ caused by the temperature gradient and the heat flux $\mathbf{J}^{(x)}_q$ due to the Dufour, or diffusion-thermo effect, which arises from concentration and pressure gradients. While this second term is generally believed to be negligible [13, 14], we include it here for completeness

$$\mathbf{J}'_q = \mathbf{J}^{(c)}_q + \mathbf{J}^{(x)}_q \qquad (37)$$

where $\mathbf{J}^{(c)}_q$ is given by the Fourier law

$$\mathbf{J}^{(c)}_q = -k\nabla T. \qquad (38)$$

The expression for the mass diffusion flux, $\mathbf{J}_k$, in a multi-component system can also be expressed as a sum of contributions [13, 14]

$$\mathbf{J}_k = \mathbf{J}^{(x)}_k + \mathbf{J}^{(P)}_k + \mathbf{J}^{(F)}_k + \mathbf{J}^{(T)}_k \qquad (39)$$

where $\mathbf{J}^{(x)}_k$ is the ordinary diffusion flux attributable to the concentration gradients of the species present in the mixture, $\mathbf{J}^{(P)}_k$ denotes diffusion due to pressure gradients, $\mathbf{J}^{(F)}_k$ represents forced diffusion due to an external force (this vanishes identically if gravity is the only external field [14] which we assume applies here), $\mathbf{J}^{(T)}_k$ is the contribution due to thermal diffusion (Soret effect) caused by the temperature gradient.

The Dufour and Soret effects represent coupling between heat and mass transfer, but for most common situations these effects, as well as the pressure diffusion term and the forced diffusion term, can be neglected [13, 14]. We shall make this assumption in this section. In addition we assume that the pressure gradient and external forces are negligible in evaluating the diffusion entropy generation rate, so that Prigogine's theorem is applicable.

Under these restrictions, the molar diffusion flux $\bar{\mathbf{J}}^*_k$, for a component k in a fluid mixture [13], can be expressed in terms of the effective binary diffusivity, $\mathscr{D}_{km}$ as

$$\bar{\mathbf{J}}^*_k = -c\mathscr{D}_{km}\nabla x_k. \qquad (40)$$

In addition we shall use the following expression for the molar chemical potential [16]:

$$\bar{\mu}_k = \bar{\mu}^0_k(T, P) + \bar{R}T \ln(\gamma_k x_k) \qquad (41)$$

where γ_k is the activity coefficient. For simplicity we consider the mixture to be an ideal solution, so $\gamma_k = 1$. Then we have

$$(\nabla\bar{\mu}_k)_{T,P} = \frac{\bar{R}T}{x_k}\nabla x_k \qquad (42)$$

and it then follows from equations (35) and (40) that

$$\sigma'_{\mathrm{d}} = \bar{R}c\sum_{k=1}^{K} \frac{\mathscr{D}_{km}}{x_k}(\nabla x_k)^2. \qquad (43)$$

Alternatively, we can use equation (25) to first rewrite equation (35) and then apply equation (42)

$$\sigma'_{\mathrm{d}} = -\frac{1}{T}\sum_{k=1}^{K-1} \bar{\mathbf{J}}^*_k \{(\nabla\bar{\mu}_k)_{T,P} - (\nabla\bar{\mu}_K)_{T,P}\}$$

$$= \bar{R}c\sum_{k=1}^{K-1} \mathscr{D}_{km}\nabla x_k \cdot \left\{ \frac{\nabla x_k}{x_k} - \frac{\nabla x_K}{x_K} \right\}. \qquad (44)$$

If, further, the total molar concentration is constant, the derivatives can be re-expressed in terms of c_k instead of x_k. We then have the volumetric rate of entropy generation, from equations (2), (5), (6), (38) and (43)

$$\sigma = \frac{k}{T^2}(\nabla T)^2 + \bar{R}\sum_{k=1}^{K} \frac{\mathscr{D}_{km}}{c_k}(\nabla c_k)^2 - \frac{1}{T}\mathbf{P}^{\mathrm{v}} : \nabla\mathbf{v}. \qquad (45)$$

The principal difference between this equation and the expressions used by San *et al.* [5, 6] and Bejan [1, 8] is that here there is no coupling term of the type $\nabla T \cdot \nabla c_k$. The reasons are discussed above in Section 4. In addition we have kept the sum over components, k, explicitly. Below we show that, except in the limiting case of a very dilute binary system, all terms should be retained in the diffusion sum. Again we emphasize that the application of this equation is restricted to situations in which the molar concentration, c, is uniform, and in which ∇P can be neglected in the direction of mass transfer.

In general, the mass diffusion flux $\mathbf{J}_k$ can also be obtained from the generalized Fick's law [13, 14] as follows:

$$\mathbf{J}_k = \frac{c}{\bar{R}T}\sum_{j=1}^{K} M_k M_j D_{kj}\omega_j(\nabla\mu_j)_{T,P} \tag{46}$$

or

$$\mathbf{J}_k = \frac{c^2}{\rho\bar{R}T}\sum_{k=1}^{K} M_j D_{kj}x_j(\nabla\bar{\mu}_j)_{T,P}. \tag{47}$$

Here D_{kj} are multi-component diffusion coefficients having the properties [13, 14]

$$D_{kk} = 0 \tag{48}$$

and

$$\sum_{k=1}^{K}(M_k M_j D_{kj} - M_k M_i D_{ki}) = 0. \tag{49}$$

To illustrate, we consider the molar form of equation (34) and substitute for $\bar{\mathbf{J}}_k$ using equation (47)

$$\sigma'_{\mathrm{d}} = -\frac{c^2}{\rho\bar{R}T^2}\sum_{k=1}^{K}\sum_{j=1}^{K} M_j D_{kj}x_j(\nabla\bar{\mu}_j)_{T,P}\cdot(\nabla\bar{\mu}_k)_T \tag{50}$$

where the gradients may be evaluated using equation (27).

In the special case of an ideal solution, and assuming also $\mathbf{J}_k \cdot \nabla P = 0$, we may use equation (42) to calculate the gradients of the molar chemical potential in equation (50)

$$\sigma'_{\mathrm{d}} = -\frac{\bar{R}c^2}{\rho}\sum_{k=1}^{K}\sum_{j=1}^{K} M_j D_{kj}\frac{1}{x_k}\nabla x_j \cdot \nabla x_k. \tag{51}$$

Now further restrict the system to just two components, A and B. We denote the binary diffusion coefficient as $\mathscr{D}_{\mathrm{AB}} = \mathscr{D}_{\mathrm{BA}}$. In this case $\nabla x_{\mathrm{A}} + \nabla x_{\mathrm{B}} = 0$ and we can simplify the summations

$$\sigma'_{\mathrm{d}} = \frac{\bar{R}c}{x_{\mathrm{A}}x_{\mathrm{B}}}\mathscr{D}_{\mathrm{AB}}(\nabla x_{\mathrm{A}})^2 \tag{52}$$

or, if c is constant

$$\sigma'_{\mathrm{d}} = \frac{\bar{R}c}{c_{\mathrm{A}}c_{\mathrm{B}}}\mathscr{D}_{\mathrm{AB}}(\nabla c_{\mathrm{A}})^2. \tag{53}$$

This equation represents the binary mixture form for the diffusion term in equation (45). The comments made in relation to that equation apply here also.

6. HEAT–MASS TRANSFER COUPLING

The phenomena which arise in a multi-component mixture when both the concentrations and temperature are nonuniform are analysed in detail by De Groot and Mazur [11]. Here we illustrate the application of the entropy production equation in an ideal binary fluid in order to examine the role of coupling between thermal and mass diffusion in second law optimization procedures.

For our purposes here we assume that viscous phenomena can be neglected, that there are no external forces present and that the pressure is uniform. We also neglect convective phenomena and we assume that concentration gradients are small enough that the density, ρ, is uniform. We label the two components, A and B. In this example we choose to use the mass, rather than the molar representation, because the link with the equations in ref. [11] is more direct. Then proceeding from equations (2), (5), (6), (33) and (34), the volumetric rate of entropy production is

$$\sigma = -\frac{1}{T^2}\mathbf{J}'_q \cdot \nabla T - \frac{1}{T}\mathbf{J}_{\mathrm{A}} \cdot \left\{\mu^{\omega}_{\mathrm{AB}}\nabla\omega_{\mathrm{B}} - \mu^{\omega}_{\mathrm{BA}}\nabla\omega_{\mathrm{A}}\right\}. \tag{54}$$

Now because $\omega_{\mathrm{A}} + \omega_{\mathrm{B}} = 1$ then $\nabla\omega_{\mathrm{B}} = -\nabla\omega_{\mathrm{A}}$ and $\mu^{\omega}_{\mathrm{AB}} = -\mu^{\omega}_{\mathrm{AA}}$. In addition the Gibbs–Duhem relation (see equation (16)), applied at constant T and P, yields

$$(\omega_{\mathrm{A}}\,\mathrm{d}\mu_{\mathrm{A}} + \omega_{\mathrm{B}}\,\mathrm{d}\mu_{\mathrm{B}})_{T,P} = 0 \tag{55}$$

and hence, using equation (26)

$$\omega_{\mathrm{A}}\mu^{\omega}_{\mathrm{AB}} = \omega_{\mathrm{B}}\mu^{\omega}_{\mathrm{BA}}. \tag{56}$$

It follows, from equation (54) that

$$\sigma = -\frac{1}{T^2}\mathbf{J}'_q \cdot \nabla T - \frac{1}{\omega_{\mathrm{B}}T}\mu^{\omega}_{\mathrm{AA}}\mathbf{J}_{\mathrm{A}} \cdot \nabla\omega_{\mathrm{A}}. \tag{57}$$

Here $\mu^{\omega}_{\mathrm{AA}}$ can be evaluated, assuming we have an ideal fluid, by using equation (42) together with equations (9), (11) and (13)

$$\mu^{\omega}_{\mathrm{AA}} = \frac{1}{M_{\mathrm{A}}}\bar{\mu}^{x}_{\mathrm{AA}}\frac{\partial x_{\mathrm{A}}}{\partial\omega_{\mathrm{A}}} = \frac{\rho\bar{R}T}{cM_{\mathrm{A}}M_{\mathrm{B}}\omega_{\mathrm{A}}} = \frac{\bar{R}T}{\omega_{\mathrm{A}}(\omega_{\mathrm{B}}M_{\mathrm{A}} + \omega_{\mathrm{A}}M_{\mathrm{B}})}. \tag{58}$$

When we include the thermal diffusion effect and the diffusion-thermo effect, the heat flux, $\mathbf{J}'_q$, and the mass flux, $\mathbf{J}_{\mathrm{A}}$, can be expressed in the form [11]

$$\mathbf{J}'_q = -k\nabla T - \rho\omega_{\mathrm{A}}\mu^{\omega}_{\mathrm{AA}}TD''\nabla\omega_{\mathrm{A}} \tag{59}$$

$$\mathbf{J}_{\mathrm{A}} = -\rho\omega_{\mathrm{A}}\omega_{\mathrm{B}}D'\nabla T + \frac{c}{\bar{R}T}M_{\mathrm{A}}M_{\mathrm{B}}\mathscr{D}_{\mathrm{AB}}\omega_{\mathrm{B}}\mu^{\omega}_{\mathrm{BA}}\nabla\omega_{\mathrm{A}}. \tag{60}$$

When the thermal diffusion effect and diffusion-thermo effect are important, these two equations should be used in the energy and mass balance equations in order to obtain the temperature and concentration distributions. Now from the Onsager relations [11], D', the thermal diffusion coefficient, and D'', the Dufour coefficient, are equal. Here, also, the ordinary diffusion flux contribution in equation (60) derives from equation (46). It then follows from equations (56) to (60)

$$\sigma = \frac{k}{T^2}(\nabla T)^2 + \frac{2\rho^2 \bar{R} D'}{M_A M_B c}(\nabla T)\cdot(\nabla \omega_A) + \frac{\rho^2 \bar{R} \mathscr{D}_{AB}}{M_A M_B \omega_A \omega_B c}(\nabla \omega_A)^2. \quad (61)$$

Alternatively σ can be expressed in terms of molar fractions using $\nabla\omega_A = M_B \omega_A c \nabla x_A / x_A \rho$. In the case where c is constant we obtain

$$\sigma = \frac{k}{T^2}(\nabla T)^2 + 2\bar{R} D' \nabla T \cdot \nabla c_A + \frac{c \bar{R} \mathscr{D}_{AB}}{c_A c_B}(\nabla c_A)^2. \quad (62)$$

These three terms correspond, respectively, to the heat transfer irreversibility, the coupling between heat and mass transfer, and the irreversibility due to mass diffusion alone. Generally the ratio of $D'/\mathscr{D}_{AB}$, called the Soret coefficient, is of the order of 10^{-3}–10^{-5} K^{-1} in gases and liquids [11]. Thus when the temperature gradient is not steep, we can usually neglect the entropy term due to the Soret and Dufour effects compared with that due to direct mass diffusion. We note that the ratio of the heat–mass transfer coupling term to the direct diffusion term is not in accordance with the equation suggested by Bejan [1, 8]. In the limit $c_A \to 0$, $c_B \to c$, the order of magnitude of this ratio is given by

$$\frac{\text{heat–mass transfer coupling irreversibility}}{\text{mass diffusion irreversibility}} \sim \frac{D'\nabla T}{\mathscr{D}_{AB}(\nabla c_A / c_A)}$$

and this will generally be much smaller than the estimate based on equation (123) of ref. [1].

7. CONCLUSIONS

We have derived expressions for the local rate of entropy generation in a fluid mixture subject to heat and mass transfer. The analysis is based on the theory of non-equilibrium thermodynamics. The expressions have been compared with those previously obtained by San *et al.* [5, 6] and Bejan [1, 8] and we have identified a number of points which have required correction or clarification. In particular the term identified by some previous authors as a mass diffusion–heat transfer coupling effect does not exist in the present theory. In the entropy generation equation, this difference arises in the way we have evaluated $\nabla\mu_k$. The effect of this modification on subsequent equations in ref. [6] is that the cross product term in its present form, involving products of the heat and mass transfer rates, should be deleted from equations (5), (14)–(17) and (19) of that reference. This change is also required in ref. [1], equation (122), and ref. [8], equations (11.171) and (11.173).

The equations for entropy generation due to mass diffusion are given in both the specific and partial molar forms. They are simplified by considering an ideal binary fluid as an example. Additional simplifications are obtained by assuming that the pressure gradient is negligible in the direction of the diffusion flux and that the total concentration is spatially uniform. We show that, in general, all terms should be retained in the sum over diffusion currents. We also find that our diffusion terms reduce to those obtained in refs. [1, 5, 6, 8] only in the limit where the molar concentration of one species is much greater than the other.

We have obtained an expression for the entropy generation rate due to mass diffusion–heat transfer coupling. This term involves the thermal diffusion coefficient, D', rather than the mass diffusivity. We show that the magnitude of this contribution to the entropy generation rate is likely to be small compared with the cross-effect term previously presented in refs. [1, 5, 6, 8]. For instance, the cross-effect determined by San *et al.* [6], in a numerical example of heat and mass transfer in laminar flow in a two-dimensional duct, influenced the total rate of entropy production by approximately 3%. In that example, therefore, the expression for the cross-effect obtained here is likely to be negligible.

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ANALYSE SELON LA SECONDE LOI DES PHENOMENES COUPLES DE TRANSFERT DE CHALEUR ET DE MASSE

Résumé—On dérive des expressions pour la création d'entropie due aux mécanismes de transfert de chaleur et de masse dans un fluide à plusieurs composants. Elles montrent que la création d'entropie a été calculée de façon incorrecte dans des publications récentes. Cette contribution est nulle bien que soient inclus les effets de la diffusion thermique. On identifie des restrictions à l'applicabilité des expressions utilisées récemment pour la création d'entropie due au transfert de masse. Un fluide binaire idéal est considéré pour illustrer l'analyse dans la limite où le gradient de pression est faible dans la direction du flux diffusionnel.

ANALYSE DES GEKOPPELTEN WÄRME- UND STOFFÜBERGANGS MIT HILFE DER ENTROPIE

Zusammenfassung—Für die Entropieerzeugung bei Vorgängen mit Wärme- und Stofftransport in Mehrstoff-Fluiden werden Gleichungen abgeleitet. Diese zeigen, daß die Entropieerzeugung bei gekoppeltem Wärme- und Stofftransport in den kürzlich veröffentlichten Arbeiten aufgrund des Kopplungseffektes falsch berechnet wurde. Dieser Beitrag tritt nur dann in Erscheinung, wenn die thermische Diffusion und die Kopplungseffekte explizit in die theoretische Beschreibung einbezogen werden. Die Einschränkungen bei der Anwendbarkeit der kürzlich veröffentlichten Beziehungen für die Entropieerzeugung bei Stofftransport werden dargelegt. Ein ideales Zweistoffgemisch wird verwendet, um die Analyse für den Fall zu veranschaulichen, bei dem der Druckgradient in Richtung des Diffusionsstroms klein ist.

ПРИМЕНЕНИЕ ВТОРОГО ЗАКОНА ТЕРМОДИНАМИКИ ДЛЯ АНАЛИЗА ЯВЛЕНИЙ СОВМЕСТНОГО ТЕПЛО- И МАССОПЕРЕНОСА

Аннотация—Выведены выражения для производства энтропии, вызванного процессами тепло- и массопереноса в многокомпонентной жидкости. Полученные выражения показывают, что в предыдущих публикациях пройзводство энтропии за счет взаимосвязанного тепло- и массопереноса рассчитано неверно. Этот вклад равен нулю, если термодиффузия и диффузионный термоэффект не учитываются в явной форме. Установлены пределы применимости выражений, используемых ранее для определения производства энтропии за счет массопереноса. Анализ иллюстрируется на примере идеальной бинарной жидкости в случае малого градиента давления в направлении диффузионного потока.