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# Entropy Production during Inter Diffusion under Internal Stress

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**Abstract.** A theory of stress and elastic deformation during interdiffusion is presented. We show its consistency with the general Darken analysis and linear irreversible thermodynamics. Special consideration is given to the local entropy production. We derive the expression for the rate of entropy production during interdiffusion and present the practical computations of the internal energy and entropy densities and the entropy production. It is shown, that the entropy produced by the diffusion of mass is positive, $A^s \geq 0$, and it does not depend on the frame of reference. The paper spans the gap between the Darken method, the linear irreversible thermodynamics and treatments by Larché, Cahn and Stephenson.

**Keywords.** entropy, entropy production, linear irreversible thermodynamics; interdiffusion; mechano-chemistry, volume continuity equation.

**PACS.** 05.70.-a, 05.70.Ln, 66.30.Ny, 82.60.-s, 46.25.-y, 46.35.+z

**1. Introduction.** In 1902, Gibbs described a mechanism by which the entropy could increase toward its equilibrium value in mechanical systems obeying Newton's equations [1]. The entropy production fascinates many physics researches, moreover in the past ten years there has been renewed interest in thermodynamics of heat engines; many papers address issues of maximum power, maximum efficiency and minimum entropy production both from practical and theoretical point of view [2 - 6]. Providing a microscopic expression for the entropy production has been one of the grand aims of statistical mechanics, going back to the seminal work of Boltzmann. However, both the range of validity of the second law and of its proposed derivations have, from the very beginning, generated discussion and controversy [7].

The deformation during diffusion was investigated by Stephensohn [8]. He noted that when the components have different partial molar volumes or diffusion coefficients their simultaneous diffusion produce the imbalance in the volume transport which generate the elastic strain and internal stress. His theoretical framework shows the evolution of the stress fields during diffusion despite the



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implicit non-compressible conditions. Recently, the special consideration is given to the generation of internal stress and vacancy chemical potential [9]. The relaxation of such potential occurs via plastic deformation and vacancy formation and annihilation. Svoboda and Fischer distinguish between interstitial and substitutional components and vacancies, including the role of non-ideal vacancy source and sink activity. This concept considers the interaction of the diffusion process with the deformation process. The stress tensor and corresponding elastic strain energy represent the additional mechanical driving force for diffusion and generation/annihilation of vacancies.

The purpose of this paper is to develop the method that takes into account the both effects of stress and the component chemical potential terms in the diffusion potentials as well as relaxation of these terms, the resulting convective mass transport and the entropy production. Following Stephenson we do not postulate the site conservation and consider multicomponent system. The method differs from the already published treatments [8], particularly in allowing the compressible elastic deformation and the effective use of the volume continuity equation [10, 13]. We show the general and exact mathematical description of the entropy production rate in the multicomponent, compressible solution which is valid for arbitrary initial conditions. The results are presented describing the entropy production in arbitrary binary diffusion couple. It is shown that the entropy production rate during diffusion is positive, does not depend on the frame of reference and depends on the initial conditions. Moreover, we show the deformation of the sample and the hydrostatic pressure field within the diffusion couple.

**2. Model.** The Liouville transport theorem is a key mathematical tool used in this work to obtain the volume continuity equation and other conservation laws. It generalizes the Gauss-Ostrogradzki theorem and consequently can be applied for the vector fields (momentum, energy and entropy conservation in this work) [11].

We consider a solid solution at constant temperature, $T = const$, and in a closed system, $m_1, ..., m_r = const$, where $m_i$ represent a constant mass of the components.

**2.1. Entropy – general description.** By the second law of thermodynamics the entropy, *s*, of the mixture contained by $|\Omega|$, $|\Omega| = \bigcup_i |\Omega_i| \subset \mathbb{R}^3$ denote the volume occupied by the mixture at time *t*, is affected by the local entropy sources, $A^s$, (due to the friction, diffusion, heat transport etc.) [1, 12]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|} s\rho \,\mathrm{d}|\Omega| = \frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|} \sum_i s_i \rho_i \,\mathrm{d}|\Omega_i| = \int_{|\Omega|} \left(A^s - \mathrm{div} J^s\right) \mathrm{d}|\Omega| \qquad (1),$$

where $J^s$ is entropy flux, $\rho$ and $\rho_i$ denote the overall and components mass densities in the mixture and the entropy density is a sum of all components $\rho s = \sum_i \rho_i s_i$ .



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We assume, that $|\Omega_i| \subseteq \mathrm{R}^3$ represents any domain of the three-dimensional space and $\upsilon_i$ is the velocity field defining the set $|\Omega_i|$. From the Liouville theorem the following identity holds

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|}\sum_i s_i\rho_i\,\mathrm{d}|\Omega_i| = \int_{|\Omega_i|}\left(\sum_i \frac{\partial s_i\rho_i}{\partial t} + \sum_i \mathrm{div}\left(s_i\rho_i\upsilon_i\right)\right)\mathrm{d}|\Omega_i|. \tag{2}$$

Combining Eqs. (1) and (2) and omitting the integrals the differential form of general equation for the entropy density follows:

$$\sum_i \frac{\partial s_i\rho_i}{\partial t} + \sum_i \mathrm{div}\left(s_i\rho_i\upsilon_i\right) + \mathrm{div}J^s = A^s \tag{3}$$

**2.2. Entropy when diffusion is not negligible.** The thermodynamics postulates the following relation defining the entropy per mass unit, $s$ [1]:

$$s = s\left(u, \Omega^m, N_1^m, N_2^m, \ldots, N_r^m\right),$$

where $u, \Omega^m, N_i^m$ denote the internal energy, the mixture specific volume per mass unit and the mass fraction ($N_i^m = \rho_i / \rho$), respectively. Multiplying the entropy by mixture density and splitting over the components results in partial Gibbs relation [13]:

$$T\rho_i s_i = \rho_i u_i - \rho_i \mu_i, \tag{4}$$

where $T$ is temperature and $\mu_i$ denotes the diffusion potential, $\mu_i = \mu_i^{ch} + \Omega_i^m p$ [1, 13]. The differential of Eq. (4) is given by the relation:

$$Ts_i\frac{\partial\rho_i}{\partial t} + T\rho_i\frac{\partial s_i}{\partial t} + \rho_i s_i\frac{\partial T}{\partial t} = \rho_i\frac{\partial u_i}{\partial t} + u_i\frac{\partial\rho_i}{\partial t} - \mu_i\frac{\partial\rho_i}{\partial t} - \rho_i\frac{\partial\mu_i}{\partial t}. \tag{5}$$

Rearranging and combining with Gibbs equation, Eq. (4), we get:

$$T\rho_i\frac{\partial s_i}{\partial t} = \rho_i\frac{\partial u_i}{\partial t} - \rho_i\frac{\partial\mu_i}{\partial t} - \rho_i s_i\frac{\partial T}{\partial t}, \tag{6}$$

summing Eqs. (6) over all of the components and multiply by $\rho^{-1}$, becomes:

$$T\sum_i N_i^m\frac{\partial s_i}{\partial t} = \sum_i N_i^m\frac{\partial u_i}{\partial t} - \sum_i N_i^m\frac{\partial\mu_i}{\partial t} - s\frac{\partial T}{\partial t}. \tag{7}$$

Using the Gibbs-Duhem relation, $s\mathrm{d}T + \sum_i N_i^m \mathrm{d}\mu_i = 0$, we get:

$$T\sum_i N_i^m\frac{\partial s_i}{\partial t} = \sum_i N_i^m\frac{\partial u_i}{\partial t} \tag{8}$$

which satisfies the second law of thermodynamics [1].

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**2.3. Energy conservation law.** According to the principle of the energy conservation, the overall energy of the mixture contained by $|\Omega|$ is affected by the energy flow into the volume $|\Omega|$ through its boundary $\partial|\Omega|$ [1]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|}\rho e\,\mathrm{d}|\Omega| = \frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|}\sum_i \rho_i e_i\,\mathrm{d}|\Omega_i| = -\int_{|\Omega|}\mathrm{div}J^e\mathrm{d}|\Omega|, \tag{9}$$

where $J^e$ is the total energy flux through the mixture boundary. From the Liouville theorem the following identity follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|}\sum_i \rho_i e_i\,\mathrm{d}|\Omega_i| = \int_{|\Omega_i|}\left(\sum_i \frac{\partial \rho_i e_i}{\partial t} + \sum_i \mathrm{div}\left(\rho_i e_i \upsilon_i\right)\right)\mathrm{d}|\Omega_i|. \tag{10}$$

Introducing Eq. (10) into (9) and omitting the integrals the differential form of energy conservation in the mixture follows:

$$\sum_i \frac{\partial \rho_i e_i}{\partial t} + \sum_i \mathrm{div}\left(\rho_i e_i \upsilon_i\right) = -\mathrm{div}J^e. \tag{11}$$

The component overall energy per mass unit, $e_i$, includes the kinetic, internal and potential contributions:

$$\rho_i e_i = \frac{1}{2}\rho_i \upsilon_i^2 + \rho_i u_i + \rho_i V^{ext}, \tag{12}$$

where the internal energy, $u_i$, follows from the Gibbs relation, (4):

$$u = \sum_i N_i^m u_i \quad \text{where} \quad u_i = Ts_i + \mu_i. \tag{13}$$

The total energy flux, $J^e$, includes the flux due to the mechanical work performed on a mixture, $p\mathbf{I}\cdot\upsilon$, and a heat flow, $J^q$:

$$J^e = p\mathbf{I}\cdot\upsilon + J^q, \tag{14}$$

where $p$ is hydrostatic pressure, $\mathbf{I}$ represents the identity tensor and $\upsilon$ denotes the overall volume velocity, $\upsilon = \sum_i \rho_i \Omega_i^m \upsilon_i$.

Using Eqs. (11), (12) and (14) the balance equation for the overall energy becomes:

$$\sum_i \frac{\partial\left(\frac{1}{2}\rho_i \upsilon_i^2 + \rho_i u_i + \rho_i V^{ext}\right)}{\partial t} + \sum_i \mathrm{div}\left(\frac{1}{2}\rho_i \upsilon_i^2 \upsilon_i + \rho_i u_i \upsilon_i + \rho_i V^{ext}\upsilon_i\right) = -\mathrm{div}\left(p\mathbf{I}\cdot\upsilon + J^q\right). \tag{15}$$

Assuming here the time independent external forcing $(\partial V^{ext}/\partial t = 0)$, the internal energy conservation law becomes:

$$\sum_i \frac{\partial \rho_i u_i}{\partial t} + \sum_i \mathrm{div}\left(\rho_i u_i \upsilon_i\right) = -\mathrm{div}\left(p\mathbf{I}\cdot\upsilon + J^q\right) - \frac{1}{2}\sum_i \frac{\partial \rho_i \upsilon_i^2}{\partial t} - \frac{1}{2}\sum_i \mathrm{div}\left(\rho_i \upsilon_i^2 \upsilon_i\right) \tag{16}$$

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**2.4. Equation of motion.** By Newton's law the rate of momentum change equals the overall force, $F=\sum_i F_i$, acting on the mass in $|\Omega|$ [1]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|}\rho\upsilon^m\,\mathrm{d}|\Omega|=\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|}\sum_i\rho_i\upsilon_i\,\mathrm{d}|\Omega_i|=\int_{|\Omega_i|}\sum_i F_i\mathrm{d}|\Omega_i|\,. \tag{17}$$

The rate of momentum of the mixture contained by $|\Omega|$ is affected by the force of elastic stress $\sum_i \mathrm{div}\left(\Omega_i^m\rho_i\,p\mathbf{I}\right)$ and external force $-\sum_i\rho_i\,\mathrm{grad}\,V^{ext}$ where $V^{ext}$ is external potential (i.e. gravitational field):

$$F=\sum_i F_i=\sum_i\mathrm{div}\left(\Omega_i^m\rho_i\,p\mathbf{I}\right)-\sum_i\rho_i\,\mathrm{grad}\,V^{ext}\,, \tag{18}$$

where $p\mathbf{I}=\boldsymbol{\sigma}:[0,\infty)\times\mathbb{R}^3\to L\left(\mathbb{R}^3,\mathbb{R}^3\right)$ is the elastic stress tensor and $L\left(\mathbb{R}^3,\mathbb{R}^3\right)$ is the space of linear mappings from $\mathbb{R}^3$ to $\mathbb{R}^3$. In Eq. (18) we postulate that the ratio of the partial elastic stress tensor of the *i*-th component $(\boldsymbol{\sigma}_i)$ to the overall elastic stress tensor $(\boldsymbol{\sigma})$ equals the ratio of volume occupied by *i*-th component in one mole of the mixture to the overall volume of the mixture: $\boldsymbol{\sigma}_i\boldsymbol{\sigma}^{-1}=\rho_i\Omega_i^m\mathbf{I}$. Thus we have ($\sum_i\rho_i\Omega_i^m=\rho\,\Omega^m=1$):

$$\boldsymbol{\sigma}_i=\rho_i\Omega_i^m\boldsymbol{\sigma} \tag{19}$$

and consequently: $\boldsymbol{\sigma}=\sum_i\boldsymbol{\sigma}_i=\sum_i\rho_i\Omega_i^m\boldsymbol{\sigma}$.

The Liouville theorem when the momentum is considered implies the following identity:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|}\rho_i\upsilon_i\,\mathrm{d}|\Omega_i|=\int_{|\Omega_i|}\left(\frac{\partial\rho_i\upsilon_i}{\partial t}+\mathrm{div}\left(\rho_i\upsilon_i\upsilon_i\right)\right)\mathrm{d}|\Omega_i|. \tag{20}$$

Combining Eqs. (17), (18) and (20) and omitting the integrals the differential form of partial equation of motion follows:

$$\frac{\partial\rho_i\upsilon_i}{\partial t}+\mathrm{div}\left(\rho_i\upsilon_i\upsilon_i\right)=\mathrm{div}\left(\Omega_i^m\rho_i\,p\mathbf{I}\right)-\rho_i\,\mathrm{grad}\,V^{ext} \tag{21}$$

By summing Eqs. (21) for all components we get overall equation of motion in all media in which diffusion is non-negligible:

$$\sum_i\frac{\partial\rho_i\upsilon_i}{\partial t}+\sum_i\mathrm{div}\left(\rho_i\upsilon_i\upsilon_i\right)=\mathrm{div}\,p\mathbf{I}-\rho\,\mathrm{grad}\,V^{ext}\,. \tag{22}$$

**2.5. Pressure definition.** We take into account the case when overall dilatation, $e^t$, is a result of stress, $e^\sigma$, and of the interdiffusion[1] (Darken velocity):

$$e^t=e^\sigma+e^D\,, \tag{23}$$

[1] It can be visualized as a spatially non-uniform Darken drift velocity, e.g., in a case of the stress free interdiffusion when $\Omega=f\left(N_1,\ldots,N_r\right)$.



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where $e = \mathrm{trace}\varepsilon$ and $\varepsilon$ denotes strain tensor.

The overall strain tensor, $\varepsilon^t$, and the overall displacement vector $\mathbf{u}$ related by:

$$\varepsilon^t = \frac{1}{2}\left(\mathrm{grad}\mathbf{u} + \mathrm{grad}\mathbf{u}^T\right). \tag{24}$$

From Eq. (24) it follows that the overall dilatation is defined by:

$$e^t = \mathrm{div}\mathbf{u}. \tag{25}$$

The elastic dilatation, $e^\sigma$, equals [14]:

$$e^\sigma = -\frac{3(1-2\nu)}{E}p. \tag{26}$$

The Darken strain tensor, $\varepsilon^D$, and the Darken displacement vector $\mathbf{u}^D$ are related by:

$$\varepsilon^D = \frac{1}{2}\left(\mathrm{grad}\mathbf{u}^D + \left(\mathrm{grad}\mathbf{u}^D\right)^T\right). \tag{27}$$

From Eq. (27) the Darken dilatation is defined by:

$$e^D = \mathrm{div}\mathbf{u}^D. \tag{28}$$

From Eq. (23) it follows:

$$\frac{\partial e^t}{\partial t} = \frac{\partial e^D}{\partial t} + \frac{\partial e^\sigma}{\partial t}. \tag{29}$$

Combining Eqs. (25), (26), (28) and (29):

$$\mathrm{div}\upsilon = \mathrm{div}\upsilon^D - \frac{3(1-2\nu)}{E}\frac{\partial p}{\partial t}, \tag{30}$$

where $\upsilon = \partial\mathbf{u}/\partial t$ and $\upsilon^D = \partial\mathbf{u}^D/\partial t$.

**2.6. Volume Continuity Equation.** The volume is not conserved, however the partial molar volumes obey the Euler relation:

$$\sum_i \frac{\Omega_i^m}{\Omega^m} N_i^m = \Omega^m \rho = 1. \tag{31}$$

The mixture volume, is the property transported by the velocity field of every mixture component contained by $|\Omega|$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|} \rho\Omega^m \,\mathrm{d}|\Omega| = \frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega_i|} \sum_i \rho_i\Omega_i^m \,\mathrm{d}|\Omega_i| = \frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|} \mathrm{d}|\Omega| \tag{32}$$

During an arbitrary transport process when volume is affected by the distribution of every mixture component and the stress field (the temperature is not considered here), from the Liouville theorem it follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{|\Omega|} \rho\Omega^m \,\mathrm{d}|\Omega| = \int_{|\Omega|}\left(\frac{\partial\rho\Omega^m}{\partial t} + \mathrm{div}\left(\rho\,\Omega^m\upsilon\right)\right)\mathrm{d}|\Omega|. \tag{33}$$



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Combining Eqs. (32) and (33) the Volume Continuity Equation (VCE) follows:

$$\frac{\mathrm{d}|\Omega|}{\mathrm{d}t} = \int_{|\Omega|} \left( \frac{\partial \rho \Omega^m}{\partial t} + \mathrm{div}\left( \rho\, \Omega^m \upsilon \right) \right) \mathrm{d}|\Omega|. \tag{34}$$

We consider here a multicomponent solution in a closed system, $m_1,...,m_r = const$, where partial molar volumes and elastic properties do not depend on composition, $\Omega_i \neq f\left(N_1,...,N_r\right)$. Thus, the volume can be only affected by the external stress:

$$\mathrm{d}|\Omega|/\mathrm{d}t = \int_{\partial|\Omega|} \upsilon^\sigma \,\mathrm{d}x. \tag{35}$$

Thus, introducing Eq. (35) into (34) the differential form of VCE follow:

$$\frac{\partial \rho \Omega^m}{\partial t} + \mathrm{div}\left( \rho\, \Omega^m \upsilon \right) = \mathrm{div}\,\upsilon^\sigma. \tag{36}$$

Introducing Euler relation, Eq. (31) we can calculate the Darken velocity, $\upsilon^D$, of the mixture:

$$\rho\, \Omega^m \upsilon = \upsilon^D + \upsilon^\sigma + \sum_i \rho_i \Omega_i^m \upsilon_i^d = \upsilon^\sigma, \tag{37}$$

where $\upsilon_i^d$ is diffusion velocity defined by proper constitutive equation (section 2.8) and $\upsilon^\sigma$ is a velocity generated by external elastic deformation.

**2.7. Mass conservation law.** The mass of the mixture component, $m_i(t)$, contained in $|\Omega_i|$ at the moment $t$ equals:

$$m_i(t) = \int_{|\Omega_i|} \rho_i \mathrm{d}|\Omega_i| \tag{38}$$

The principle of conservation of mass states that the mass contained by $|\Omega_i|$ is conserved[2]. Thus,

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{|\Omega_i|} \rho_i \mathrm{d}|\Omega_i| = 0. \tag{39}$$

By the Liouville theorem:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{|\Omega_i|} \rho_i \,\mathrm{d}|\Omega_i| = \int_{|\Omega_i|} \left( \frac{\partial \rho_i}{\partial t} + \mathrm{div}\left( \rho_i \upsilon_i \right) \right) \mathrm{d}|\Omega_i|. \tag{40}$$

Combining Eqs. (39) and (40) and omitting the integrals results in local mass conservation laws for all components:

$$\frac{\partial \rho_i}{\partial t} + \mathrm{div}\left( \rho_i \upsilon_i \right) = 0. \tag{41}$$

[2]To simplify the relations, in this work we do not consider the chemical and/or nuclear reactions in the mixture, i.e., we do neglect the local sources and sinks of mass.



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**2.8. The diffusion velocity** in a case when no external forces are considered is given by the Nernst-Planck equation [15, 16]:

$$\upsilon_i^d = -B_i \operatorname{grad} \mu_i = -B_i \operatorname{grad}\left(\mu_i^{ch} + \Omega_i^m p\right), \tag{42}$$

where $\mu_i$ is the diffusion potential and $B_i$ denotes the mobility of the $i$-th component.

We consider mixture were the drift velocity is a result of the external elastic deformation $\left(\upsilon^\sigma\right)$ and diffusion (the Darken drift, $\upsilon^D$). Thus, the component velocities are defined by:

$$\upsilon_i = \upsilon_i^d + \upsilon^{drift} \quad \text{where} \quad \upsilon^{drift}(t,x) = \upsilon^\sigma(t,x) + \upsilon^D(t,x). \tag{43}$$

**2.9. Entropy production and entropy flux.** Entropy production and entropy flux can be calculated by comparing Eqs. (3) and (8). Introducing the mass conservation law, Eq. (41) into overall entropy formula, Eq. (3), we get:

$$\sum_i \rho_i \frac{\partial s_i}{\partial t} + \sum_i \rho_i \upsilon_i \operatorname{grad} s_i + \operatorname{div} J^s = A^s. \tag{44}$$

On the other side, upon introducing the internal energy conservation law, Eq. (16) and equation of motion, Eq. (21) into Eq. (8) we get:

$$\sum_i \rho_i \frac{\partial s_i}{\partial t} = -\frac{1}{T}\sum_i \rho_i \upsilon_i \operatorname{grad} u_i - \sum_i \frac{1}{T}\operatorname{div}\left(p\mathbf{I}\cdot\upsilon + J^q\right) - \frac{1}{T}\sum_i \upsilon_i \operatorname{div}\left(\Omega_i^m \rho_i\, p\mathbf{I}\right). \tag{45}$$

Rearranging the final entropy balance equation can be written in terms of fluxes and forces as:

$$\begin{aligned} &\sum_i \rho_i \frac{\partial s_i}{\partial t} + \sum_i \rho_i \upsilon_i \nabla s_i + \operatorname{div}\left(\frac{J^q + p\upsilon}{T}\right) = \\ &= \sum_i \upsilon_i \nabla\left(\frac{\Omega_i^m \rho_i\, p}{T}\right) + J^q \nabla \frac{1}{T} - \sum_i \rho_i \upsilon_i^d \nabla \frac{\mu_i}{T} + \sum_i \rho_i \upsilon_i^d u_i \nabla \frac{1}{T}. \end{aligned} \tag{46}$$

Comparing Eqs. (44) and (46) the local entropy production rate and the entropy flux equal:

$$A^s = \sum_i \upsilon_i \nabla\left(\frac{\Omega_i^m \rho_i\, p}{T}\right) + J^q \nabla \frac{1}{T} - \sum_i \rho_i \upsilon_i^d \nabla \frac{\mu_i}{T} + \sum_i \rho_i \upsilon_i^d u_i \nabla \frac{1}{T}, \tag{47}$$

$$J^s = \frac{J^q + p\upsilon}{T}. \tag{48}$$

Above relations allow to formulate the initial boundary-value problem of diffusion.

**3. Formulation of the free-boundary value problem of interdiffusion under the stress field.**

**Data:**

1) $M_i \in (0,\infty)$, $\quad i = 1,\ldots,r$ $\quad$ the molecular mass of the i-th component

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2) $\Omega_i \in (0,\infty)$ the molar volume of the i-th component, $i=1,2,\ldots,r$

3) $|\Omega| \subset \mathbb{R}^3$ the volume occupied by the mixture at time $t$

4) $D_i : \bigtimes_{k=1}^{r} [0,1] \to [0,\infty)$ the diffusion coefficient of the i-th component, $\bigtimes_{k=1}^{r}$ denotes the Cartesian product

5) $t \in (0,\infty)$ duration of the process

6) $T \in (0,\infty)$ the constant process temperature

7) $E \in (0,\infty)$ the Young modulus

8) $v \in (0,\infty)$ the Poisson number

**The unknowns:**

1) $\rho_i : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to [0,\infty)$ density of the i-th component, where $i = 1,\ldots,r$.

2) $\upsilon^{drift} : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to \mathbb{R}^3$ drift velocity of the mixture

3) $p : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to \mathbb{R}$ pressure of the mixture

4) $u : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to \mathbb{R}$ internal energy of the mixture

5) $s : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to \mathbb{R}$ entropy of the mixture

6) $A^s : \bigcup_{0\le t^* \le t} \{t^*\} \times |\Omega| \to \mathbb{R}$ entropy production in the mixture

**Physical laws:**

1) $\dfrac{\partial \rho_i}{\partial t} = -\operatorname{div}\left(\rho_i \upsilon_i^d + \rho_i \upsilon^{drift}\right)$, the mass conservation law for the i-th component.

2) $\dfrac{\mathrm{d}|\Omega|}{\mathrm{d}t} = \int_{|\Omega|} \operatorname{div}\upsilon \,\mathrm{d}x = \int_{|\Omega|} \operatorname{div}\upsilon^{\sigma} \,\mathrm{d}x$, The volume continuity equation (VCE)

3) $\operatorname{div}\upsilon = \operatorname{div}\upsilon^D - \dfrac{3(1-2v)}{E}\dfrac{\partial p}{\partial t}$ evolution of pressure in the mixture

4) $\rho_i \dfrac{\partial u_i}{\partial t} + \rho_i \upsilon_i \operatorname{grad} u_i = -\Omega_i^m \rho_i \, p\mathbf{I} : \operatorname{grad}\upsilon_i$ the internal energy conservation of the $i$-th component, where the overall internal energy of the mixture is $\rho u = \sum_i \rho_i u_i$ .

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5) $Ts_i = u_i - \mu_i$ partial Gibbs-Duhem relation. The overall entropy of the mixture is calculated from: $\rho s = \sum_i \rho_i s_i$ .

6) $A^s = \sum_i \upsilon_i \mathrm{grad}\left(\frac{\Omega_i^m \rho_i \ p}{T}\right) - \sum_i \rho_i \upsilon_i^d \mathrm{grad}\frac{\mu_i}{T}$, the entropy production rate in case of isothermal process (i.e. the temperature gradient is negligible).

**Initial conditions:**

1) $\overset{0}{\rho}_i : |\Omega| \to [0,\infty)$ the initial density distribution of the *i*-th component

2) $\overset{0}{c} = \sum_i \overset{0}{\rho}_i / M_i$ the initial overall molar concentration of the mixture

3) $\overset{0}{p} \in \square$ the initial pressure field

4) $\overset{0}{u}_i \in \square$ the initial internal energy

**Boundary conditions:**

1) $\rho_i \upsilon_i^d (t) \square n = 0 \quad \text{on} \ \partial|\Omega|$ the diffusion flux of the *i*-th component at the mixture boundary, where *n* represents the unit vector normal to the boundary i.e., in the closed system analyzed here, the mass flow through the mixture boundaries does not occur.

2) $\frac{\partial p}{\partial n} = \mathrm{grad}\, p \square n = 0 \quad \text{on} \ \partial|\Omega|$ the pressure derivative at the boundaries equals zero, i.e., there is no external forcing.

**4. Results.** In this section we present the internal energy evolution and the entropy generated when diffusion is not negligible. The data used to simulate the mechano-chemical diffusion process in the arbitrary binary alloy are shown in Table 1. We consider an ideal solid solution $(a_i = c_i)$ in which the diffusivities of components differ.

Temperature: 1273 [K]

Young modulus: 100 [GPa]

Poisson number: 0.3

Simulation time: 100 [h]

Sample length: 1 [cm]

**Stress effect on interdiffusion.** In Fig. 1 the impact of the pressure field on diffusion is presented. The solid line shows the concentration profile when the stress (pressure) field is considered

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$\left(\mu_i = \mu_i^{ch} + \Omega_i^m p = RT \ln c_i + \Omega_i^m p\right)$, the dash line present the calculations without the stress field $\left(\mu_i = RT \ln c_i\right)$. It can be seen that stress field slows down the diffusion process.

Spatial distribution of the: a) drift velocity, b) pressure field, c) internal energy and d) entropy in the binary alloy is shown in Fig. 2.

The method allows calculating the entropy production during diffusion process, Fig. 3. The entropy produced by the mass diffusion is positive, $A^s \geq 0$, and it does not depend on the frame of reference, Eq. (47).

The initial conditions markedly affect the entropy produced during diffusion process. Figure 4 presents the evolutions of concentration for four different diffusion couples shown in Tables 1 and 2.

Figure 5 shows the comparison of the drift velocity, pressure, internal energy and entropy in case of different initial composition. The different behavior of the evolution e.g. pressure profile can be observed.

Finally in Fig. 6 we show that the entropy produced by the mass diffusion in the case of different initial conditions is positive, $A^s \geq 0$.

**5. Summary.** We have shown the consistency of the generalized Darken method (bi-velocity method) with the linear irreversible thermodynamics. We defined the material fixed frame of reference and effectively used the volume continuity equation. The resulting system of physical laws, initial and boundary conditions (i.e., the initial boundary value problem) allows using the bi-velocity method to model the complex mechano-chemical processes. We derived the expressions for the rate of entropy production during interdiffusion and presented the evolution of the internal energy, entropy and entropy production. It is shown, that the entropy produced by the diffusion of mass is positive, $A^s \geq 0$, and it does not depend on the frame of reference.

The presented method spans the gap between the Darken method, linear irreversible thermodynamics and treatments by Larché, Cahn and Stephenson. We have shown its effective use to predict *1*) the time dependence of the mixture concentration, *2*) the internal pressure field generated during diffusion, *3*) the energy and entropy of the mixture and *4)* the entropy production term.

In this work we considered the binary solid solution. It ternary and higher systems the multiple diffusion paths are possible and often observed. The minimization of the entropy production can allow to solve this long lasting problem, i.e., can in a unique way define the evolution of the diffusion paths.

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Table 1. The data used to simulate the diffusion under the stress field in arbitrary binary alloy.

| Component | Component diffusivity, $D_i$ [cm$^2$s$^{-1}$] | Molar mass, $M_i$ [g mol$^{-1}$] | Molar volume at $p = 10^5$ Pa $\Omega_i$ [cm$^3$mol$^{-1}$] |
|---|---|---|---|
| 1 | $1.0 \cdot 10^{-9}$ | 100 | 10 |
| 2 | $1.0 \cdot 10^{-10}$ | 200 | 20 |

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Table 2. Initial concentrations in the diffusion couples shown in Figs. 4-6.

| | Component concentration, at. % | |
|---|---|---|
| Diffusion couple | $x \in [-0.5, 0)$ [cm] | $x \in [0, 0.5]$ [cm] |
| 1 | 0 | 100 |
| 2 | 10 | 100 |
| 3 | 50 | 100 |
| 4 | 75 | 100 |

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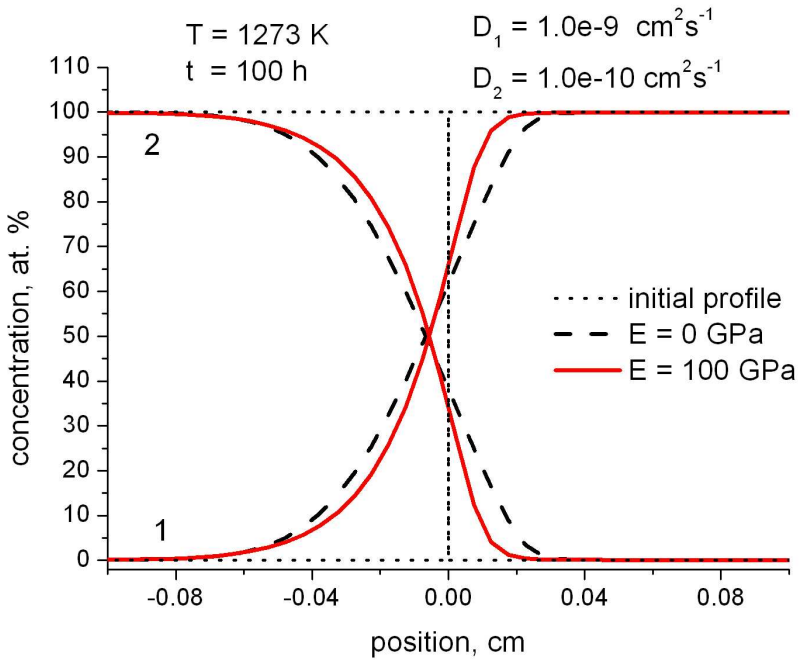


Figure 1. The influence of the internal stress field on diffusion in the binary alloy.
289x202mm (150 x 150 DPI)

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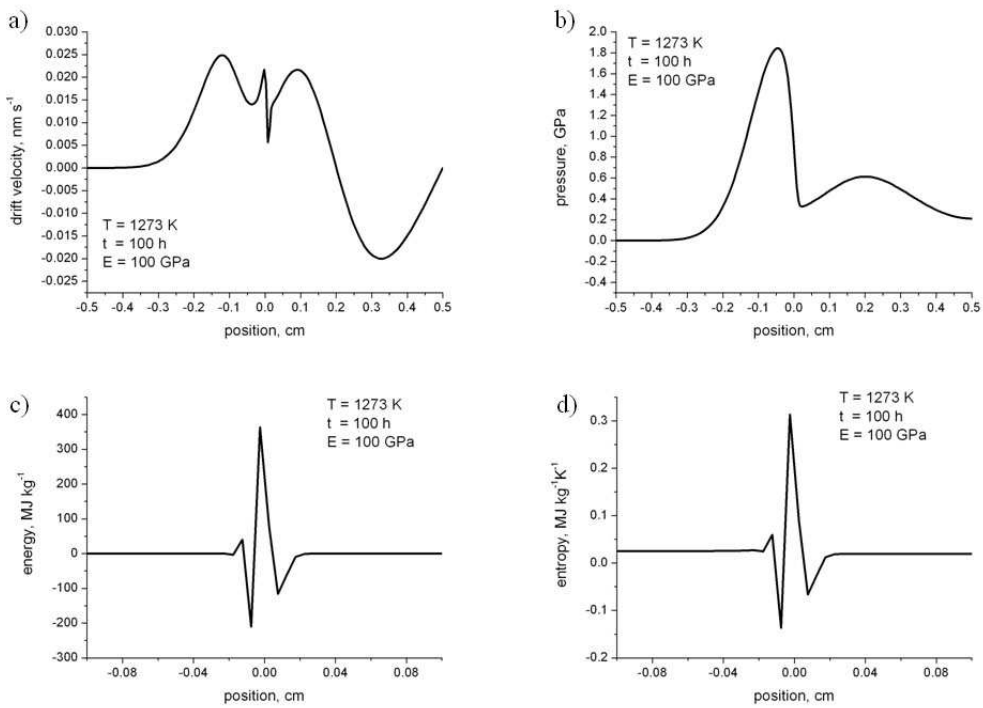


Figure 2. Spatial distribution of the: a) drift velocity, b) pressure field, c) internal energy and d) entropy in the binary alloy.
330x238mm (72 x 72 DPI)

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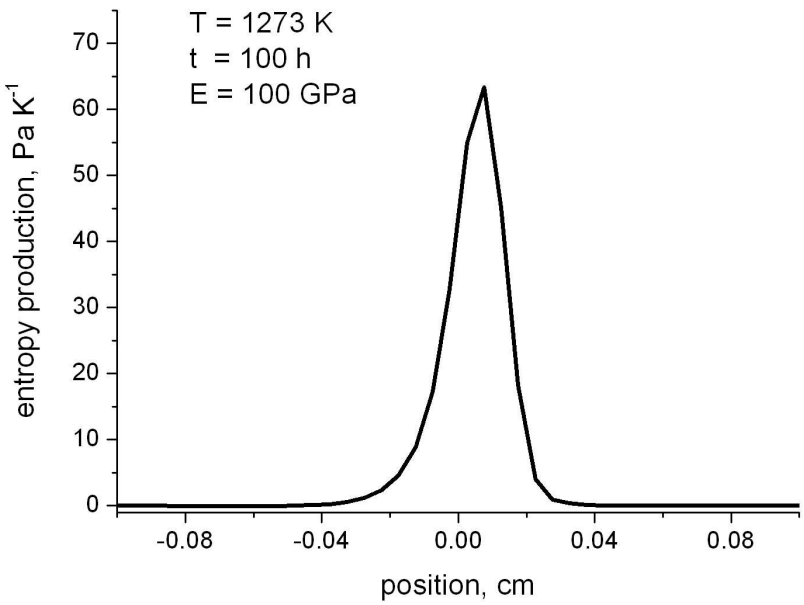


Figure 3. Spatial distribution of the entropy production during diffusion process in the binary alloy.
289x202mm (150 x 150 DPI)

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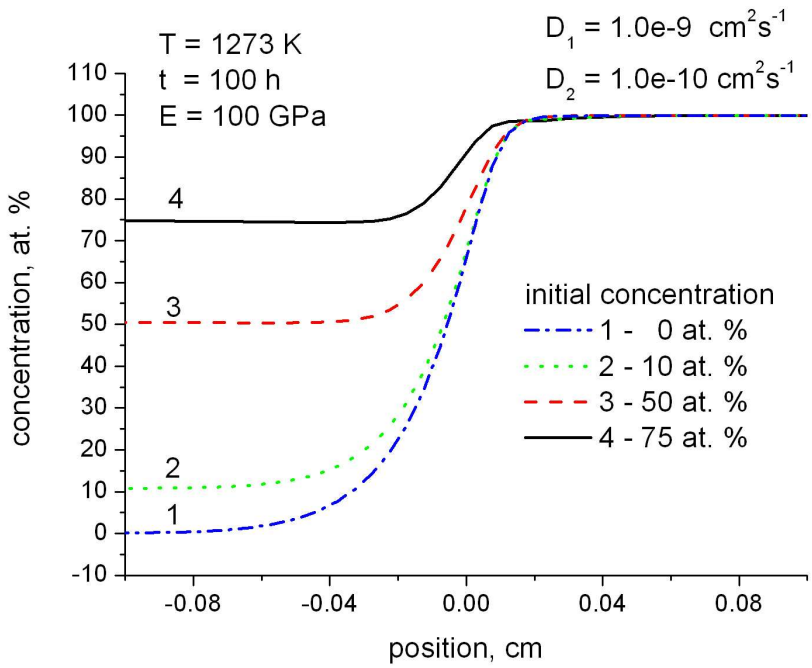


Figure 4. The concentration profiles during diffusion under the stress field for different initial conditions.
289x202mm (150 x 150 DPI)

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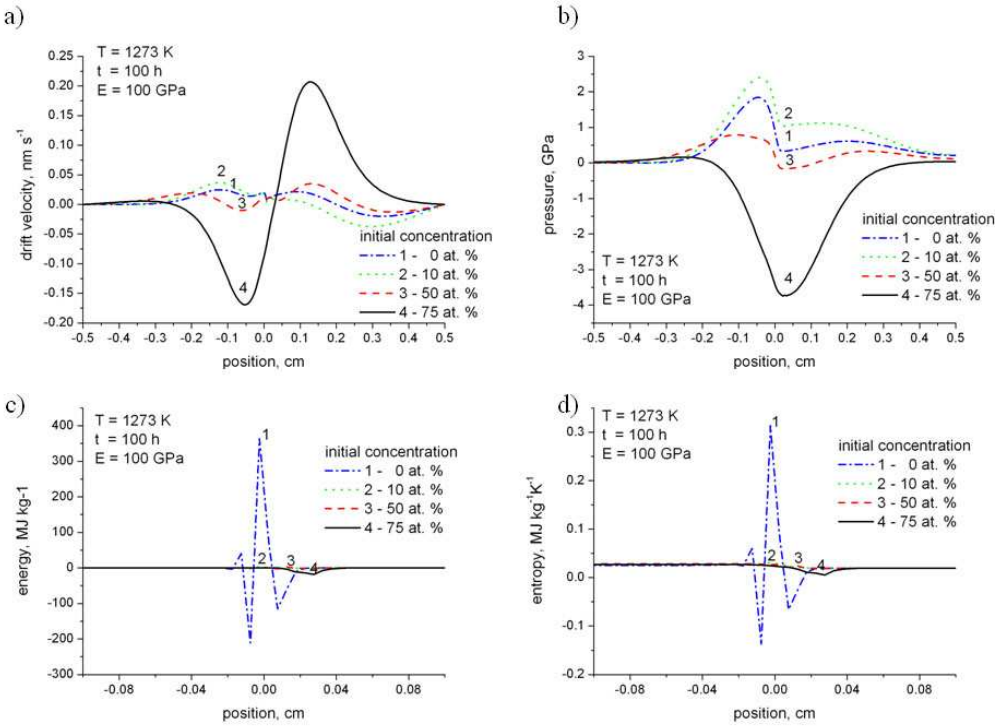


Figure 5. The evolution of the a) drift velocity, b) pressure field, c) internal energy and d) entropy in the binary diffusion couple fir the different initial conditions shown in Table 2.
323x237mm (72 x 72 DPI)

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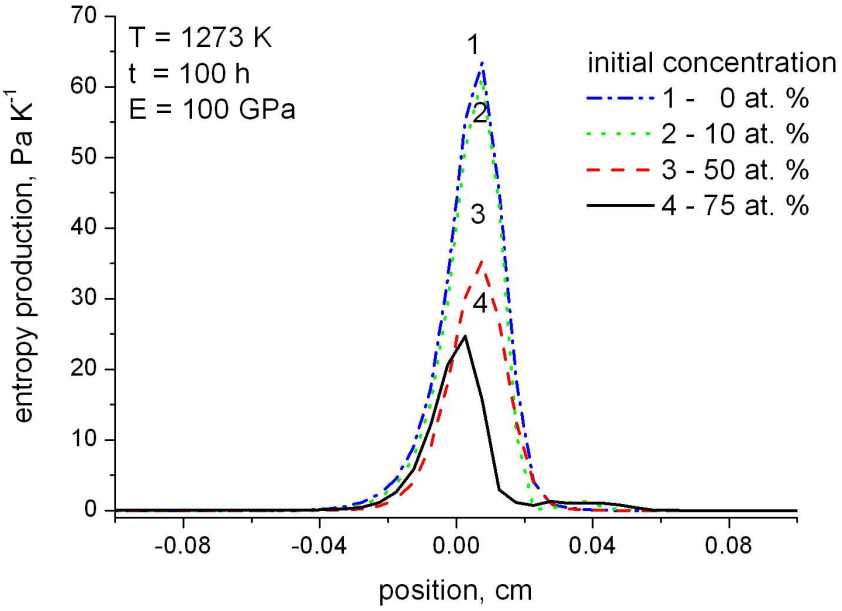


Figure 6. The entropy production generated by diffusion under the stress field for different initial conditions.
289x202mm (150 x 150 DPI)

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