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Examples of thermodynamic models of freezing of pore water in porous materials

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Examples of Thermodynamic Models of Freezing of Pore Water in Porous Materials

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Abstract

Examples of how to develop models using the physical balance principles defined in the mixture theory, together with the use of the second axiom of thermodynamics and proper constitutive relations.

1 A few remarks on heat transfer and phase change problems

In this section, the classical heat conduction equation for a single temperature θ of the mixture will be derived using a simplified version of the energy balance equation together with required constitutive relations. A more detailed description of the problem, involving the concepts of the free energy density ψ_a and the entropy η_a for the constituents in a mixture, will also given to show the difficulties involved in improving the assumptions.

In the so-called Stefan's problem, a modified version of the linear classical heat conduction equation is used to track the propagation of a freezing or melting front of a pure material undergoing a phase change. Essentially, six material parameters are used in this approach. However, the formation of ice in a porous material with a wide range of pore sizes filled, or partly filled, with a pore solution and containing different chemical components does not satisfy the basic assumptions introduced for solving the Stefan's problem. The important difference between the Stefan's problem and the freezing of liquid water in a porous medium will be discussed.

The most important phase change problem in the area of durability of porous building materials is probably the formation of ice in the pore system. Ice may cause damage such as internal micro-cracks and scaling of material surfaces. A problem of special interest, in this context, is the formation of ice in combination with deicing salts. This damage differs from the one which arises when a pore solution freezes without the presence of external salts.

To obtain the standard heat conduction equation, the internal energy ε must be constituted with the material constant C and the temperature θ, as

$$\varepsilon = C\theta \tag{1}$$

where C represents the specific heat capacity of the material considered.

The heat flux q_x in a one-dimensional case is constituted by a temperature gradient assumption and the material constant λ called the conductivity as

$$q_x = -\lambda \frac{\partial \theta}{\partial x} \tag{2}$$

The body force of all constituents $\mathbf{b}_a$, the influence of the term including the stress tensor and the velocity gradient for the mixture $\mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L}$, and the external heat supply for the mixture r are all assumed to be negligibly small quantities compared to the others in the energy balance equation. The simplified energy balance equation in one dimension becomes

$$\rho \frac{\partial \varepsilon}{\partial t} = -\frac{\partial q_x}{\partial x} - \rho \dot{x}_x \frac{\partial \varepsilon}{\partial x} \tag{3}$$

where ρ is the mass density of the mixture and $\dot{x}_x$ is the mean velocity of the mixture.

If the constitutive relations (1) and (2) are introduced into the simplified energy balance equation (3),

$$\rho C \frac{\partial \theta}{\partial t} = \lambda \frac{\partial^2 \theta}{\partial x^2} - \rho C \dot{x}_x \frac{\partial \theta}{\partial x} \tag{4}$$

is obtained. If the mean velocity $\dot{x}_x$ vanish, the equation (4) represents the standard heat conduction problem, which must be supplemented with boundary conditions in terms of temperature and/or a heat flux. Furthermore, the initial conditions must be specified.

In the Stefan's problem, the mean velocity of the mixture $\dot{x}_x$ vanish, and the material parameters C and λ are assumed to be functions of the temperature itself. Thus, the temperature field in a domain where a phase change

occurs can be solved, and assure energy balance, with a non-linear version of (4). The governing equation in the Stefan's problem can be obtained by introducing the constitutive relation of a rate type for the internal energy as

$$\dot{\varepsilon} = C(\theta)\,\dot{\theta} \tag{5}$$

The heat flux is constituted as

$$q_x = -\lambda(\theta)\,\frac{\partial \theta}{\partial x} \tag{6}$$

Furthermore, the divergence of the heat flux can be expressed by

$$\frac{\partial q_x}{\partial x} = -\frac{\partial}{\partial x}\left(\lambda(\theta)\,\frac{\partial \theta}{\partial x}\right) = -\lambda(\theta)\left(\frac{\partial \theta}{\partial x}\right)^2 - \lambda(\theta)\,\frac{\partial^2 \theta}{\partial x^2} \tag{7}$$

It is assumed that

$$\left(\frac{\partial \theta}{\partial x}\right)^2 \ll 1 \tag{8}$$

With (5), (6), (8), and (3), the non-linear version of the standard heat equation becomes

$$\rho C(\theta)\frac{\partial \theta}{\partial t} = \lambda(\theta)\frac{\partial^2 \theta}{\partial x^2} \tag{9}$$

if the velocity of the mixture $\dot{x}$ vanish.

Whenever the phase change temperature θ_f is reached, the material parameter $C(\theta)$ will exhibit a discontinuous jump. This is due to the latent heat effect L (J/kg), since the latent heat L is adsorbed or emitted during the phase change.

Integrating around the phase change temperature θ_f gives

$$L = \int_{\theta_f^-}^{\theta_f^+} C(\theta)\,d\theta \tag{10}$$

which is a material constant for pure materials undergoing a certain phase change. It is important that certain material parameters are known when the Stefan's problem is applied to liquid water and ice. These are the specific heat capacities of liquid water C_l and ice C_{ice}, and the 'specific' heat capacity during the phase change C_L. The C_L value represents the latent heat effect calculated from the material constant L together with an assumption of a small temperature interval, during which the phase change is supposed to

Table 1: Material constants for water and ice used in the Stefan's problem.

Constant	Value	Remarks
C_l	$1.762 \cdot 10^3$ (J/kg/K)	*Specific heat capacity, liquid water*
C_{ice}	$4.226 \cdot 10^3$ (J/kg/K)	*Specific heat capacity, ice*
λ_l	2.220 (J/s/m/K)	*Conductivity of liquid*
λ_{ice}	0.556 (J/s/m/K))	*Conductivity of ice*
L	$333.6 \cdot 10^3$ (J/kg)	*Latent heat of fusion*
θ_f	273.15 (K)	*Transition temperature*
$\Delta\theta_f$	$\sim 0.01 - 0.0001$ (K)	*Used to compute C_f from L*

occur. Furthermore, two different constant values of the conductivity λ are adopted, that is, the conductivity of liquid water λ_l and ice λ_{ice}. Compare the data for water and ice in Table 1.

Within the assumed phase change temperature interval, the conductivity λ is often assumed to be linear between the values λ_l and λ_{ice}. The change of the mass density of the mixture ρ is, however, normally incorporated into the C values. Besides, the pressure effects upon the formation of ice are ignored in the Stefan's problem.

By solving the non-linear equation (9) with the above-mentioned material parameters, a discontinuous freezing or melting front can be followed for all kinds of variation of the boundary conditions, simply by checking at which locations in the domain the temperature is below the specified temperature θ_f. Numerical methods solving the equation (9) have been proposed, e.g. compare (Steen Krenk, Lars Damkilde).

However, an inherent problem when studying porous materials with a wide range of pore sizes is that not all of the liquid water present in the pore system is transformed from water to ice when a certain freezing temperature θ_f is reached, as assumed in the Stefan's problem. In order to use the energy balance concept to calculate the mass density of ice $\rho_{ice}(\mathbf{x}, t)$ formed in a porous material, modifications to the classical Stefan's problem must be introduced.

It is believed that liquid water present in different pore sizes in a saturated porous material will exhibit different freezing temperatures θ_f, i.e. a scatter of different latent heat effects at different temperatures must be overcome. The initial mass concentration of liquid water c_l, however, give no information as to how this liquid water is distributed among the different pore sizes in

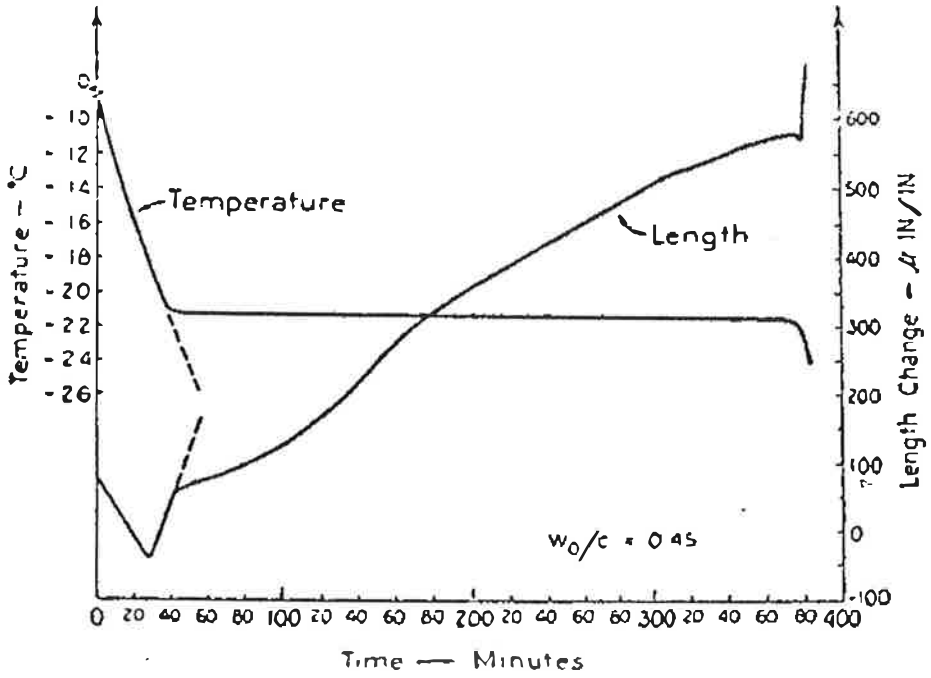

Figure 1: *Effect of holding temperature constant after freezing starts in a relatively dense paste, [Powers].*

a representative material volume (REV). That is, some kind of geometrical consideration in addition to the porosity n and the specific surface area a must be introduced, and some relation must give the distribution of liquid water in this geometry.

By using for example the Kelvin equation together with quantitative measurements or microscope studies the pore distribution curves can be evaluated. The pore distribution curves indicate of which pore size radii r_p the total porosity consists. The most simple distribution function of liquid water for such a geometry is the assumption that a given mass concentration of liquid water c_l occupies the smallest pores completely. In other words, if half of the porosity in a porous medium consists of pores smaller than a given value r_{p50} and the degree of saturation is 50%, all these pores are assumed to be completely filled with liquid and all the remaining pores, larger or equal to r_{p50} will be assumed to be completely dry. A simple way to improve this

assumption is by distinguishing between adsorbed water molecules and liquid water stuck to the pore walls due to capillary condensation. That is, the adsorbed water can be assumed to be distributed among the different pore sizes in relation to its corresponding envelope-specific surface areas.

Furthermore, a function relating the freeze temperature θ_f to the different pore size radii r_p must be introduced in order to evaluate the function $C(\theta)$ for a specific material with a known pore size distribution. The latent heat L is, however, not a constant even when the fusion of ice in a normal condition is considered. Thus, supercooled or undercooled water will exhibit different latent heat L at different temperatures. At 273.15 (K), 263.15 (K), and 253.15 (K), the latent heat of fusion of ice is 333.6 (kJ/kg), 284.8 (kJ/kg), and 241.4 (kJ/kg) respectively (Hobbs).

There are many other important effects which must not be overlooked. One of them is that the liquid water (on a microscopic scale) present in the largest pores (having a certain known θ_f) will form ice when the ice formation is nucleated. This first ice formed is, however, believed to attract water from neighboring pores with smaller radii than that contained in the ice in its vapor and liquid phases. This phenomenon may significantly change the assumed distribution function of liquid water during the freezing process. The equation (9) together with assumptions of pore size distributions can not be used alone to calculate the mass density of ice $\rho_{ice}(\mathbf{x}, t)$. The effects of water from neighboring pores or from the surroundings being drawn towards ice islands created in the pore system is often referred to as cryogenic suction or cryosuction, e.g. compare (Ozawa). Cryosuction is explained by the difference in the free energy of ice at a certain temperature and unfrozen water at the same temperature.

Furthermore, if the attraction of water-vapor towards the ice islands in the pore system is significant, the amount of vapor to be converted to ice, i.e. the sublimation, might be of importance. The latent heat of fusion is approximately 12% of the latent heat of sublimation at 273.15 (K) and at atmospheric pressure.

It is noted that calorimeter measurements can not reveal the amount of ice formed in the pore system directly without making assumptions of the involved latent heat of fusion and sublimation at different temperatures and at different mass concentrations of water in the pore system. One problem to be considered is for example that the latent heat of fusion of capillary water is different from the latent heat of fusion of adsorbed and capillary-condensed water at a certain temperature. Furthermore, the latent heat of sublimation

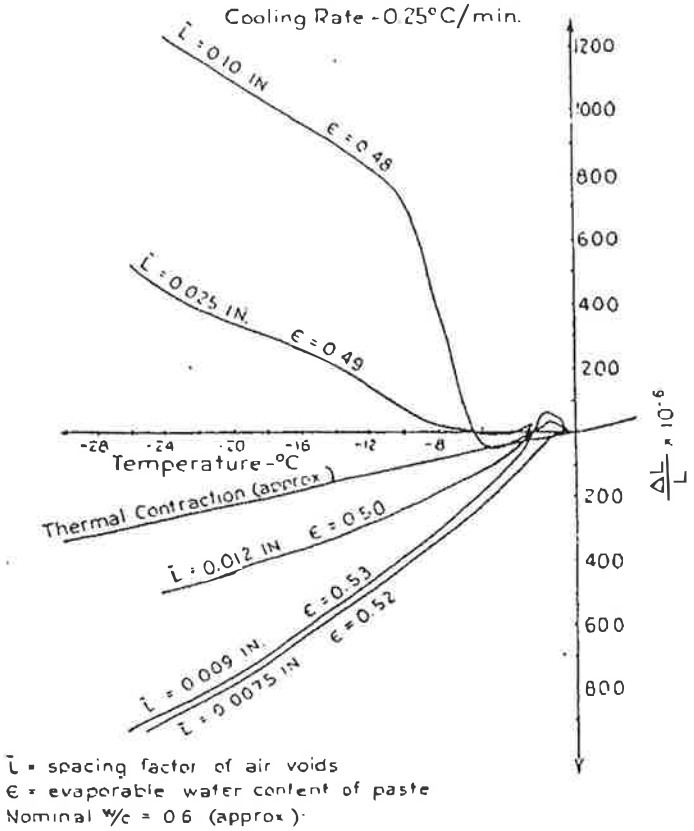

Figure 2: *Effect of entrained air and the spacing factor, [Powers].*

and the fusion can not be distinguished, since the calorimeter measures the total response in terms of heat output or heat input.

Since the ice grown from the vapor phase is very different in structure than ice grown from bulk water, the sublimation phenomenon may have important consequences in terms of micro-cracking of the solid material. Besides, as the growth of ice becomes diffusion-controlled, the time scale of vapor flow towards ice islands and the degree of external cooling rate become important. If, for example, the external cooling rate is fairly rapid, the diffusion-controlled sublimation is supposed to be small, and if the external cooling rate is slow, the ice growth due to sublimation (or, rather, damages caused by sublimation) might prevail, compare Figure 1.

In a situation, where the diffusion-controlled ice growth, i.e. the sublimation, is active, different ice crystals will be formed depending on the degree of supercooling. The various ice crystals growing at different temperatures in a diffusion cloud chamber are: (*i*) hexagonal plates from 273.15 to 270 K, (*ii*) needles from 270 to 268 (K), (*iii*) prismatic columns from 268 to 265 K, (*iv*) hexagonal plates from 265 to 261 (K), (*v*) dendrites from 261 to 257 (K), (*vi*) hexagonal plates from 257 to 248 (K) (Hobbs). The saturation pressure of the vapor involved in the sublimation has been shown not to affect the overall formation pattern of these different crystals. Temperature, it seems, is the main factor. Due to the different geometrical shape of these crystals, they might cause different kinds of damage to the solid. Dendrites and needles might be the most damaging products formed due to the needle-like shape of these crystals.

The thermomechanical problem of ice growth in concrete is often studied by measuring the length changes due to a temperature depression and due to ice growth in the pore system, see Figures 1 and 2, (Powers). In order to evaluate such measurements, the concept of stress and strain in the porous material must be introduced.

By combining the first and second axiom of thermodynamics, the thermomechanical coupling can be studied. Here, the free specific energy potential ψ_a and the entropy η_a are used as constitutive dependent properties. Indeed the thermodynamic properties ψ_a and η_a can be quite generally constituted, and therefore a more general energy equation than (4) can be obtained. This general equation is believed to be more adequate when phase change problems are studied, where factors other than temperature itself will affect the thermodynamic state variables ε_a or ψ_a and η_a. Similar approaches have been proposed, e.g. compare (Coussy). The Helmholz's free energy ψ and the entropy η are often introduced as well when studying thermomechanical coupling, e.g. compare (Lemaitre).

For example, the mass concentration of dissolved chloride ions and pore water present in different pore sizes will be factors affecting the freezing temperature. Hence, the thermodynamic state variables ε_a, ψ_a and η_a will also be affected. The derivation of a more general equation than (9) is not straightforward, since such formulations often include so-called internal variables. Furthermore, problems associated with the fulfillment of the second axiom of thermodynamics must also be dealt with. However, it will be shown that it is possible to study freeze-thaw problems in porous materials using the concept of mixture theory. Here, two different strategies to obtain an equa-

tion dealing with heat conductivity and chemically reacting constituents will be presented. It will be shown that different thermodynamic laws can be defined due to the second axiom of thermodynamics. The definitions of the thermodynamic laws do not follow directly from the second axiom of thermodynamics, but rather from the combination of this axiom and the choice of constitutive relations.

Consider the second axiom of thermodynamics (compare, the chapter Theory of Mixtures), as expressed in terms of the Helmholz's free energy ψ_a and the entropy η_a, i.e.

$$\begin{aligned} 0 \quad \leq \quad & -\sum_{a=1}^{\Re} \rho_a \psi_a' - \sum_{a=1}^{\Re} \rho_a \eta_a \dot{\theta} + \sum_{a=1}^{\Re} \mathrm{tr} \mathbf{T}_a^{\mathrm{T}} \mathbf{L}_a \\ & - \sum_{a=1}^{\Re} \left(\mathbf{q}_a + \rho_a \theta \eta_a \mathbf{u}_a \right) \cdot \mathrm{grad}\left(\theta\right) / \theta \\ & - \sum_{a=1}^{\Re} \mathbf{u}_a \cdot \hat{\mathbf{p}}_a - \sum_{a=1}^{\Re} \hat{c}_a \left(\psi_a + \tfrac{1}{2} u_a^2 \right) \end{aligned} \tag{11}$$

Two examples will be studied, both based on the assumption that the Helmholz's free energy depends only on the temperature and the mass density, that is

$$\psi_a = \psi_a \left(\theta, \rho_a\right) \tag{12}$$

At first, the partial hydrostatic pressures π_a will be defined with the help of the Helmholz's free energy ψ_a described through (12). In order to define the pressure, consider the derivative of (12), i.e.

$$\rho_a \psi_a' = \rho_a \frac{\partial \psi_a}{\partial \theta} \theta' + \rho_a \frac{\partial \psi_a}{\partial \rho_a} \rho_a' \tag{13}$$

It should further be noted that $\mathrm{div}\, \mathbf{x}_a' = \mathrm{tr}\left(\mathrm{grad}\, \mathbf{x}_a'\right) = \mathrm{tr}\, \mathbf{L}_a$, which allows the mass balance to be written

$$\rho_a' = -\rho_a \,\mathrm{tr}\, \mathbf{L}_a + \hat{c}_a \tag{14}$$

(compare, the chapter Theory of Mixtures). If (13) and (14) are combined

$$\rho_a \psi_a' = \rho_a \frac{\partial \psi_a}{\partial \theta} \theta' - \rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} tr\, \mathbf{L}_a + \rho_a \frac{\partial \psi_a}{\partial \rho_a} \hat{c}_a \tag{15}$$

is yielded.

Only the terms in the second axiom of thermodynamics containing the term $\mathbf{L}_a$ will be considered at this stage. It is concluded that the first term and the third term in (11) together with (15) result in a validation of the following restriction:

$$\sum_{a=1}^{\Re} \mathrm{tr}\left(\rho_a^2 \frac{\partial \psi_a}{\partial \rho_a}\mathbf{I} + \mathbf{T}_a^{\mathrm{T}}\right)\mathbf{L}_a \geq 0 \tag{16}$$

Since $\mathbf{L}_a$ is arbitrary, it follows that the parenthesis in equation (16) must be equal to zero in order to satisfy the part of the inequality containing the velocity gradient term. This makes it possible to define the thermodynamic law for the stress tensor as

$$\mathbf{T}_a = -\rho_a^2 \frac{\partial \psi_a}{\partial \rho_a}\mathbf{I} \tag{17}$$

The stress tensor is described with the hydrostatic pressure only, i.e.

$$\mathbf{T}_a = -\pi_a \mathbf{I} \tag{18}$$

Following the thermodynamic law (17) as well as (18), the expression for the hydrostatic pressure can be written as

$$\pi_a = \rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \tag{19}$$

This means for example that the choice $\psi_a(\theta, \rho_a) = R\theta \ln \rho_a$ gives the expression $\pi_a = R\theta\rho_a$ which is the ideal gas law.

The following discussion will concern two constituents denoted 1 and 2. For simplicity, the following restrictions will be assumed:

$$\begin{matrix} \mathbf{x}_1'(\mathbf{x}, t) = \mathbf{0} \\ \mathbf{x}_2'(\mathbf{x}, t) = \mathbf{0} \end{matrix} ; \tag{20}$$

This means that also the velocity of the mixture $\dot{\mathbf{x}}$ and the diffusion velocities $\mathbf{u}_a$ are restricted to be zero. That is, a problem with heat conduction and chemical reactions will be studied, in which the constituents have zero velocities and where the hydrostatic pressures for the constituents are defined by $\pi_1 = \rho_1^2 \partial\psi_1/\partial\rho_1$ and $\pi_2 = \rho_2^2 \partial\psi_2/\partial\rho_2$, i.e. by the equation (19).

The fifteen unknown properties in both the test problems for the heat conducting and reacting constituents 1 and 2 are:

$$\begin{matrix} \rho_1(\mathbf{x}, t) \\ \rho_2(\mathbf{x}, t) \end{matrix} ; \quad \theta(\mathbf{x}, t); \quad \begin{matrix} \hat{c}_1(\mathbf{x}, t) \\ \hat{c}_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \eta_1(\mathbf{x}, t) \\ \eta_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \psi_1(\mathbf{x}, t) \\ \psi_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \mathbf{q}_1(\mathbf{x}, t) \\ \mathbf{q}_2(\mathbf{x}, t) \end{matrix} ; \tag{21}$$

where the independent variables are the mass densities ρ_1 and ρ_2 and the temperature θ. The rest of the properties listed in (21) are the constitutive variables. It should be noted that the heat fluxes $\mathbf{q}_1$ and $\mathbf{q}_2$ involves three unknown properties each.

Due to the assumptions in (20), the inequality (11) is simplified to

$$-\sum_{a=1}^{2}\rho_a\dot{\psi}_a-\rho\eta\dot{\theta}-\sum_{a=1}^{2}\mathbf{q}_a\cdot\operatorname{grad}(\theta)/\theta-\sum_{a=1}^{2}\hat{c}_a\psi_a\geq 0 \tag{22}$$

where $\psi'_a=\dot{\psi}_a$ and $\mathbf{h}=\mathbf{q}_1+\mathbf{q}_2$ due to the restriction of zero velocities for the two considered constituents.

It is further assumed that the Helmholz's free energy for the constituents 1 and 2 are given as functions of the temperature and the mass densities ρ_1 and ρ_2, i.e.

$$\begin{aligned}\psi_1&=\psi_1(\theta,\rho_1)\\ \psi_2&=\psi_2(\theta,\rho_2)\end{aligned} \tag{23}$$

The entropies for the constituents 1 and 2 are assumed to depend on the same quantities, i.e.

$$\begin{aligned}\eta_1&=\eta_1(\theta,\rho_1)\\ \eta_2&=\eta_2(\theta,\rho_2)\end{aligned} \tag{24}$$

The chemical reaction rate $\hat{c}_1$ is constituted as a function of the temperature θ and the mass density of the constituents.

$$\begin{aligned}\hat{c}_1&=f_1(\theta,\rho_1,\rho_2)\\ \hat{c}_2&=f_2(\theta,\rho_1,\rho_2)\end{aligned} \tag{25}$$

At last, the heat fluxes is constituted as

$$\begin{aligned}\mathbf{q}_1&=\mathbf{f}_1(\operatorname{grad}\theta)\\ \mathbf{q}_2&=\mathbf{f}_2(\operatorname{grad}\theta)\end{aligned} \tag{26}$$

The differentiation of ψ_1 and ψ_2, given from (23), yields

$$\dot{\psi}_1=\frac{\partial\psi_1}{\partial\theta}\dot{\theta}+\frac{\partial\psi_1}{\partial\rho_1}\dot{\rho}_1 \tag{27}$$

$$\dot{\psi}_2=\frac{\partial\psi_2}{\partial\theta}\dot{\theta}+\frac{\partial\psi_2}{\partial\rho_2}\dot{\rho}_2 \tag{28}$$

The entropy η for the whole mixture is the definition

$$\rho\eta = \sum_{a=1}^{\Re} \rho_a \eta_a \tag{29}$$

If (27), (28), and (29) are introduced into the simplified inequality (22), the result is

$$-\sum_{a=1}^{2} \rho_a \left(\frac{\partial \psi_a}{\partial \theta}\dot{\theta} + \frac{\partial \psi_a}{\partial \rho_a}\dot{\rho}_a \right) - \sum_{a=1}^{2} \rho_a \eta_a \dot{\theta} - \sum_{a=1}^{2} \mathbf{q}_a \cdot \operatorname{grad}(\theta)/\theta - \sum_{a=1}^{2} \hat{c}_a \psi_a \geq 0 \tag{30}$$

The mass balance for constituents 1 and 2, is broken down to

$$\dot{\rho}_1 = \hat{c}_1 \tag{31}$$
$$\dot{\rho}_2 = \hat{c}_2 \tag{32}$$

since $\partial \rho_a / \partial t = \dot{\rho}_a$ when $\mathbf{x}'_a$ and $\dot{\mathbf{x}}$ is equal to zero, e.g. compare the chapter Theory of Mixtures. The constraint on the mass balance equation is

$$\sum_{a=1}^{2} \hat{c}_a = 0 \tag{33}$$

If the mass balance equations (31), (32), and the constraint (33) are introduced into (30),

$$-\sum_{a=1}^{2} \rho_a \left(\frac{\partial \psi_a}{\partial \theta} + \eta_a \right) \dot{\theta} - \sum_{a=1}^{2} \left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a \right) \dot{\rho}_a - \sum_{a=1}^{2} \mathbf{q}_a \cdot \operatorname{grad}(\theta)/\theta \geq 0 \tag{34}$$

is yielded. Since $\dot{\theta}$ is an arbitrary quantity, it seems natural to define the thermodynamic laws

$$\frac{\partial \psi_1}{\partial \theta} = -\eta_1; \tag{35}$$
$$\frac{\partial \psi_2}{\partial \theta} = -\eta_2; \tag{36}$$

which assure that the first terms in (34) fulfill the reduced inequality.

A so-called dissipation inequality is introduced for the second term in (33) by replacing $\dot{\rho}_1$ with $\hat{c}_1$ and also $\dot{\rho}_2$ with $\hat{c}_2$. In other words, the equations (31)

and (32) are inserted into the second term in (34). This yields the dissipation inequality

$$\varphi_{chem.} = -\sum_{a=1}^{2}\left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a\right)\hat{c}_a \geq 0 \tag{37}$$

This inequality is valid only when the velocity of both constituents is zero, i.e. when the relation $\dot{\rho}_a = \hat{c}_a$ holds for the constituents 1 and 2. The property $\varphi_{chem.}$ will be referred to as the chemical dissipation.

It can be established that the dissipation inequality (37) is positive by making a proper constitutive assumption for the rate of the chemical reaction, $\hat{c}_a$, involving rather than introducing thermodynamic definitions or laws.

To obtain a constitutive relation, which describes the reaction kinetics, (33) must be considered, which yields

$$\hat{c}_1 = -\hat{c}_2 \tag{38}$$

The chemical dissipation $\varphi_{chem.}$ for the constituents 1 and 2 then becomes

$$\varphi_{chem.} = -\sum_{a=1}^{2}\left(\rho_a \frac{\partial \psi_a}{\partial \rho_a} + \psi_a\right)\hat{c}_a = -\left(\rho_1 \frac{\partial \psi_1}{\partial \rho_1} + \psi_1 - \rho_2 \frac{\partial \psi_2}{\partial \rho_2} - \psi_2\right)\hat{c}_1 \tag{39}$$

This makes the constitutive relation describing the chemical reaction rate $\hat{c}_a$ restricted. The following natural choice appears attractive:

$$\hat{c}_1 = \dot{\rho}_1 = -G_{12}\left(\rho_1 \frac{\partial \psi_1}{\partial \rho_1} + \psi_1 - \rho_2 \frac{\partial \psi_2}{\partial \rho_2} - \psi_2\right) \tag{40}$$

where G_{12} is a positive scalar quantity denoting a material property, which describes the reaction kinetics. From (40) and (37) it is concluded that the chemical dissipation is always positive in this case, since $\varphi_{chem.}$ is a quadratic assumption. It is noted that the chemical reaction rate $\hat{c}_1$ is a function of the mass densities ρ_1 and ρ_2 and the temperature θ, compare (25). This is due to the fact that ψ_1 and ψ_2 depend on the same quantities, compare (23).

It is worth noting that (40) expresses an assumed chemical reaction rate which is proportional to the chemical potential difference between the phases 1 and 2. This can be verified by considering the definition of the chemical potential tensor $\mathbf{K}_a$, i.e.

$$\mathbf{K}_a = \psi_a \mathbf{I} - \mathbf{T}_a^{\mathrm{T}}/\rho_a \tag{41}$$

The stress tensor was assumed to be constituted with the thermodynamic pressure π_a only, i.e.

$$\mathbf{T}_a = -\pi_a \mathbf{I} = -\rho_a^2 \frac{\partial \psi_a}{\partial \rho_a} \mathbf{I} \tag{42}$$

By comparing (41) and (42) and also noting that $\mathbf{K}_a = \mu_a \mathbf{I}$ when having no mechanical pressures involved, this gives the expression for the chemical potential μ_a, as

$$\mu_a = \psi_a - \rho_a \frac{\partial \psi_a}{\partial \rho_a} \tag{43}$$

That is (43) shows that

$$\rho_1 \frac{\partial \psi_1}{\partial \rho_1} + \psi_1 - \rho_2 \frac{\partial \psi_2}{\partial \rho_2} - \psi_2 = \mu_1 - \mu_2 \tag{44}$$

which was the result to be shown.

The so-called thermal dissipation is the last term in the reduced inequality (34), i.e.

$$\varphi_{therm.} = -\frac{\sum_{a=1}^{2} \mathbf{q}_a}{\theta} . \operatorname{grad} \theta \geq 0 \tag{45}$$

If an isotropic heat flux is assumed, the thermal dissipation can be assured to be a non-negative quantity by introducing the constitutive relations

$$\mathbf{q}_1 = -\tilde{\lambda}_1 \operatorname{grad} \theta \tag{46}$$

$$\mathbf{q}_2 = -\tilde{\lambda}_2 \operatorname{grad} \theta \tag{47}$$

which means that the dissipation is quadratic in $\operatorname{grad} \theta$. Both material constants $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$ are restricted to be positive scalars. When studying anisotropic heat flux problems, i.e. using an assumption of the type $\mathbf{q}_a = -\mathbf{C}_{(\lambda)a} \operatorname{grad} \theta$, the thermal dissipation inequality, i.e. $\varphi_{therm.} \geq 0$, imposes the restriction that the conductivity tensor $\mathbf{C}_{(\lambda)a}$ must be positive definite.

From the introduced thermodynamic laws (35) and (36), the expression for the rate of change of the entropies $\dot{\eta}_a$ for the constituents 1 and 2 takes the form

$$\dot{\eta}_1 = -\frac{\partial^2 \psi_1}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_1}{\partial \theta \partial \rho_1} \dot{\rho}_1 \tag{48}$$

$$\dot{\eta}_2 = -\frac{\partial^2 \psi_2}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_2}{\partial \theta \partial \rho_2} \dot{\rho}_2 \tag{49}$$

where it is assumed that η_1 and η_2 depend on the same quantities as ψ_1 and ψ_2 do, compare (24).

In addition, the energy balance equation written in the form

$$\rho\theta\dot{\eta} + \operatorname{div}\mathbf{h} + \sum_{a=1}^{\Re}\mathbf{u}_a\cdot\hat{\mathbf{p}}_a + \sum_{a=1}^{\Re}\hat{c}_a\tfrac{1}{2}u_a^2 - \rho r \tag{50}$$
$$= -\sum_{a=1}^{\Re}(\rho_a\psi_a' + \hat{c}_a\psi_a) - \rho\eta\dot{\theta} + \operatorname{tr}\sum_{a=1}^{\Re}\mathbf{T}_a^{\mathrm{T}}\mathbf{L}_a$$

should be considered, compare chapter: Theory of Mixtures. With the constraints in (20), the simplified version of the energy equation (50) is

$$\rho\theta\dot{\eta} + \operatorname{div}\sum_{a=1}^{2}\mathbf{q}_a + \sum_{a=1}^{2}\rho_a\dot{\psi}_a + \sum_{a=1}^{2}\hat{c}_a\psi_a + \rho\eta\dot{\theta} = 0 \tag{51}$$

It follows from (29) that

$$\eta = \frac{1}{\rho}\sum_{a=1}^{\Re}\rho_a\eta_a \tag{52}$$

By the differentiation of the quantity η as

$$\dot{\eta} = \frac{1}{\rho}\sum_{a=1}^{2}(\dot{\rho}_a\eta_a + \rho_a\dot{\eta}_a) \tag{53}$$

where it should be observed that $\rho = const.$ due to the simplified mass balance equations (31) and (32) and due to (33), i.e.

$$\sum_{a=1}^{2}\hat{c}_a = \dot{\rho}_1 + \dot{\rho}_2 = \dot{\rho} = 0 \tag{54}$$

where also the mass balance for the mixture and the assumption $\dot{\mathbf{x}} = \mathbf{0}$ are used.

If the assumed expressions are introduced for $\dot{\eta}_a$ and $\dot{\psi}_a$, the energy equation (50) can be written as

$$\begin{aligned} 0 \;=\; & \theta\sum_{a=1}^{2}\left(\dot{\rho}_a\left(-\frac{\partial\psi_a}{\partial\theta}\right) + \rho_a\left(-\frac{\partial^2\psi_a}{\partial\theta^2}\dot{\theta} - \frac{\partial^2\psi_a}{\partial\theta\partial\rho_a}\dot{\rho}_a\right)\right) \\ & + \operatorname{div}\sum_{a=1}^{2}\mathbf{q}_a + \sum_{a=1}^{2}\rho_a\left(\frac{\partial\psi_a}{\partial\theta}\dot{\theta} + \frac{\partial\psi_a}{\partial\rho_a}\dot{\rho}_a\right) \\ & + \sum_{a=1}^{2}\hat{c}_a\psi_a + \sum_{a=1}^{2}\rho_a\left(-\frac{\partial\psi_a}{\partial\theta}\right)\dot{\theta} \end{aligned} \tag{55}$$

where (53), (48), and (49) together with the thermodynamic laws (35) and (36) are used. If this expression is rearranged and $\hat{c}_1$ and $\hat{c}_2$ are replaced by $\dot{\rho}_1$ and $\dot{\rho}_2$, through the use of the mass balance equations, i.e. (31) and (32), the result is

$$\begin{aligned} 0 &= \theta \sum_{a=1}^{2} \left(\dot{\rho}_a \left(-\frac{\partial \psi_a}{\partial \theta} \right) + \rho_a \left(-\frac{\partial^2 \psi_a}{\partial \theta^2} \dot{\theta} - \frac{\partial^2 \psi_a}{\partial \theta \partial \rho_a} \dot{\rho}_a \right) \right) \\ &\quad + \text{div} \sum_{a=1}^{2} \mathbf{q}_a + \sum_{a=1}^{2} \rho_a \frac{\partial \psi_a}{\partial \rho_a} \dot{\rho}_a + \sum_{a=1}^{2} \dot{\rho}_a \psi_a \end{aligned} \tag{56}$$

This expression can be referred to as a generalization of the standard heat conduction equation, e.g. compare (9).

If the Helmholz's free energies ψ_1 and ψ_2 are specified in more detail by introducing constitutive relations containing the material constants C_1, C_2, K_1, K_2, L_1 and L_2 as

$$\psi_1(\theta, \rho_1) = C_1 \theta (1 - \ln \theta) + K_1 \theta / \rho_1 + L_1 \tag{57}$$

$$\psi_2(\theta, \rho_2) = C_2 \theta (1 - \ln \theta) + K_2 \theta / \rho_2 + L_2 \tag{58}$$

where C_1 can be referred to as the heat capacity for the constituent denoted 1, K_1 represents a factor describing the dependency of the free energy on the composition of the mixture, i.e. the relation between the mass densities ρ_1 and ρ_2 during the chemical reaction or, equally, during the phase change. The material constant $L_{12} = L_1 - L_2$ represents the latent heat effect of the reaction studied.

The needed derivatives in the energy equation (56) can now be written down explicitly as

$$\frac{\partial \psi_1}{\partial \theta} = -C_1 \ln \theta + K_1 / \rho_1 \tag{59}$$

which is the expression for the entropy with an opposite sign of the constituent denoted 1. The second derivative of the Helmholz's free energy with respect to the temperature is

$$\frac{\partial^2 \psi_1}{\partial \theta^2} = -C_1 / \theta \tag{60}$$

Furthermore

$$\frac{\partial \psi_1}{\partial \rho_1} = -K_1 \theta / \rho_1^2 \tag{61}$$

is obtained, and finally

$$\frac{\partial^2 \psi_1}{\partial\theta\partial\rho_1} = -K_1/\rho_1^2 \tag{62}$$

This term can be referred to as the thermochemical coupling. That is, the constitutive relations (57) and (58) explicitly result in a predicted coupling term, which will affect the temperature distribution in the mixture.

Insertion of these assumptions into the expression (56) yields

$$\begin{aligned} 0 \;=\; & \sum_{a=1}^{2} \dot{\rho}_a \left(C_a \ln\theta - \frac{K_a}{\rho_a} \right) \theta + \sum_{a=1}^{2} \left(\rho_a C_a\right) \dot{\theta} \\ & + \sum_{a=1}^{2} \left(\frac{K_a}{\rho_a} \dot{\rho}_a \right) \theta + \operatorname{div} \sum_{a=1}^{2} \mathbf{q}_a \\ & + \sum_{a=1}^{2} \left(-\frac{K_a}{\rho_a} \dot{\rho}_a \right) \theta + \sum_{a=1}^{2} \dot{\rho}_a \left(C_a \theta \left(1 - \ln\theta\right) + \frac{K_a}{\rho_a}\theta + L_a \right) \end{aligned} \tag{63}$$

Following (46) and (47), the total heat flux $\mathbf{q}$ becomes

$$\mathbf{q} = \sum_{a=1}^{2} \mathbf{q}_a = -\left(\tilde{\lambda}_1 + \bar{\lambda}_2 \right) \operatorname{grad}\theta \tag{64}$$

If (64) is inserted into (63) and it is noted that some of the terms are canceled out, the result is

$$\sum_{a=1}^{2} \rho_a C_a \dot{\theta} - \operatorname{div}\left(\tilde{\lambda}_1 + \tilde{\lambda}_2 \right) \operatorname{grad}\theta + \sum_{a=1}^{2} \dot{\rho}_a \left(C_a\theta + L_a \right) = 0 \tag{65}$$

Furthermore, the total heat flux is assumed to be weighted with the mass densities ρ_1 and ρ_2 and with a material constant m as

$$\lambda_{tot} = \tilde{\lambda}_1 + \bar{\lambda}_2 = \left(\frac{\rho_1}{\rho} \lambda_1^m + \frac{\rho_2}{\rho} \lambda_2^m \right)^{1/m} \tag{66}$$

where $-1 \leq m \leq 1$.

It should be noted again that $\rho_2 = \rho - \rho_1$, $\rho = const.$, and that $\dot{\rho}_2 = -\dot{\rho}_1$. The heat equation (65) can then be written as

$$\left(\rho C_2 + \rho_1 \left(C_1 - C_2\right)\right) \dot{\theta} - \operatorname{div}\left(\lambda_{tot}\right) \operatorname{grad}\theta + \left(C_1 - C_2\right) \dot{\rho}_1 \theta + L_{12} \dot{\rho}_1 = 0 \tag{67}$$

where $L_{12} = L_1 - L_2$, and where it should be observed that $\dot{\rho}_1$ must be given from a constitutive relation of the type suggested in (40). This restriction is imposed on the constitutive behavior due to the second axiom of thermodynamics. If the given relations for the Helmholz free energy for the constituents are inserted into (40), the result is the expression for the assumed reaction kinetics.

The fifteen unknown properties in (21) can now be solved by using (40) and (67). That is, the temperature field $\theta(\mathbf{x}, t)$ and the two mass concentration fields $\rho_1(\mathbf{x}, t)$ and $\rho_2(\mathbf{x}, t)$ can be calculated. Note that the used equations are the two mass balance equations (31) and (32), the energy balance equation (31), the two thermodynamic laws for the constituents relating the Helmholz free energy to its corresponding entropies (35) and (36), the constitutive relation for the reaction kinetics (40) together with the restriction (33), the two constitutive relations for the heat flux vectors (46) and (47) (in all six equations are thus involved to describe the heat fluxes for the two constituents), and finally the two constitutive relations for the Helmholz free energy (57) and (58). That is, the number of unknown properties equals the number of equations introduced.

In order to illustrate that alternative constitutive equations yield different thermodynamic definitions and hence governing equations, yet another method will be examined. The same restrictions and unknown properties will be studied as in the previous example, i.e.

$$\begin{matrix} \rho_1(\mathbf{x}, t) \\ \rho_2(\mathbf{x}, t) \end{matrix} ; \quad \theta(\mathbf{x}, t) ; \quad \begin{matrix} \hat{c}_1(\mathbf{x}, t) \\ \hat{c}_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \eta_1(\mathbf{x}, t) \\ \eta_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \psi_1(\mathbf{x}, t) \\ \psi_2(\mathbf{x}, t) \end{matrix} ; \quad \begin{matrix} \mathbf{q}_1(\mathbf{x}, t) \\ \mathbf{q}_2(\mathbf{x}, t) \end{matrix} ; \tag{68}$$

There is one main difference compared to the first example, namely the constitutive relation for the reaction kinetics. The following rate type of assumption will be introduced:

$$\begin{matrix} \hat{c}_1 = f_1\left(\dot{\theta}\right) \\ \hat{c}_2 = f_2\left(\dot{\theta}\right) \end{matrix} \tag{69}$$

which can be compared with the constitutive relations used in the first example, see (21). The Helmholz free energy, the entropy and the heat flux are assumed to be dependent on the same quantities as in the first example, i.e. compare (23), (24) and (26).

The equations for $\hat{c}_1$ and $\hat{c}_2$ will be constituted as

$$\hat{c}_1 = R_1 \dot{\theta} \tag{70}$$

and

$$\hat{c}_2 = R_2\dot{\theta} \tag{71}$$

where R_1 and R_2 are the rate constants for the chemical reaction. From (33) it follows that these constants must be related as

$$R_1 + R_2 = 0 \tag{72}$$

where (33) is used. Consider, furthermore, the reduced second axiom of thermodynamics (34) together with the equations (70) and (71), i.e.

$$-\sum_{a=1}^{2}\rho_a\left(\frac{\partial\psi_a}{\partial\theta} + \eta_a + R_a\frac{\partial\psi_a}{\partial\rho_a} + \frac{R_a}{\rho_a}\psi_a\right)\dot{\theta} - \sum_{a=1}^{2}\mathbf{q}_a \cdot \operatorname{grad}(\theta)/\theta \geq 0 \tag{73}$$

where the relation $\dot{\rho}_a = \hat{c}_a$ is used.

The thermal dissipation $\varphi_{therm.}$, compare (45), is proven to be a positive quantity due to the relations (46) and (47).

In this example, the assumed reaction kinetics, i.e. (70) and (71), makes it possible to introduce the following thermodynamic definitions relating the Helmholtz free energy and the entropy for the constituents since $\dot{\theta}$ is arbitrary:

$$\frac{\partial\psi_1}{\partial\theta} + R_1\frac{\partial\psi_1}{\partial\rho_1} + \frac{R_1}{\rho_1}\psi_1 = -\eta_1 \tag{74}$$

and

$$\frac{\partial\psi_2}{\partial\theta} - R_1\frac{\partial\psi_2}{\partial\rho_2} - \frac{R_1}{\rho_2}\psi_2 = -\eta_2 \tag{75}$$

where equation (72) is used. The equations (74) and (75) are sufficient to ascertain that (73) is true. It should be noted, however, that a more general condition can be obtained if the thermodynamic definitions for the entropies for the two constituents are not separated.

A differentiation of (74) yields

$$\begin{aligned}\dot{\eta}_1 \;=\; & -\frac{\partial^2\psi_1}{\partial\theta^2}\dot{\theta} - \frac{\partial^2\psi_1}{\partial\theta\partial\rho_1}\dot{\rho}_1 - R_1\frac{\partial\psi_1}{\partial\rho_1\partial\theta}\dot{\theta} \\ & -R_1\frac{\partial^2\psi_1}{\partial\rho_1^2}\dot{\rho}_1 + \frac{R_1}{\rho_1^2}\psi_1 - \frac{R_1}{\rho_1}\frac{\partial\psi_1}{\partial\theta} - \frac{R_1}{\rho_1}\frac{\partial\psi_1}{\partial\rho_1}\end{aligned} \tag{76}$$

and a differentiation of (75) yields

$$\begin{aligned}\dot{\eta}_2 &= -\frac{\partial^2\psi_2}{\partial\theta^2}\dot{\theta} - \frac{\partial^2\psi_2}{\partial\theta\partial\rho_2}\dot{\rho}_2 + R_1\frac{\partial\psi_2}{\partial\rho_2\partial\theta}\dot{\theta} \\ &\quad + R_1\frac{\partial^2\psi_1}{\partial\rho_2^2}\dot{\rho}_2 - \frac{R_1}{\rho_2^2}\psi_2 + \frac{R_1}{\rho_2}\frac{\partial\psi_2}{\partial\theta} + \frac{R_1}{\rho_2}\frac{\partial\psi_2}{\partial\rho_2}\end{aligned} \tag{77}$$

Slightly different assumptions are introduced for $\psi_1(\theta,\rho_1)$ and $\psi_2(\theta,\rho_2)$ compared to the previous example, using

$$\psi_1(\theta,\rho_1) = C_1\theta(1-\ln\theta) + K_1\rho_1 + L_{12} \tag{78}$$

$$\psi_2(\theta,\rho_2) = C_2\theta(1-\ln\theta) + K_2\rho_2 \tag{79}$$

where C_1, C_2, K_1, K_2, and L_{12} are material constants. The derivatives of interest in the reduced energy equation (56) are

$$\frac{\partial\psi_1}{\partial\theta} = -C_1\ln\theta \tag{80}$$

and

$$\frac{\partial^2\psi_1}{\partial\theta^2} = -C_1/\theta \tag{81}$$

and finally

$$\frac{\partial\psi_1}{\partial\rho_1} = K_1 \tag{82}$$

The thermochemical coupling $\partial^2\psi_1/(\partial\theta\partial\rho_1)$ is ignored in this example, due to the structure of the constitutive relations for $\psi_1(\theta,\rho_1)$ and $\psi_2(\theta,\rho_2)$. The same type of derivatives are obtained for the constituent denoted 2. The rest of the derivatives for the constituents are equal to zero following the assumptions (78) and (79). Hence, the explicit expressions for $\dot{\eta}_1$ become

$$\begin{aligned}\dot{\eta}_1 &= \frac{C_1}{\theta}\dot{\theta} + \frac{R_1}{\rho_1^2}\left(C_1\theta(1-\ln\theta) + K_1\rho_1 + L_{12}\right) \\ &\quad + \frac{R_1C_1}{\rho_1}\ln\theta - \frac{R_1}{\rho_1}K_1\end{aligned} \tag{83}$$

For $\dot{\eta}_2$,

$$\begin{aligned}\dot{\eta}_2 &= \frac{C_2}{\theta}\dot{\theta} - \frac{R_1}{\rho_2^2}\left(C_2\theta(1-\ln\theta) + K_2\rho_2\right) \\ &\quad - \frac{R_1C_2}{\rho_2}\ln\theta + \frac{R_1}{\rho_2}K_2\end{aligned} \tag{84}$$

is obtained. The rate of change of the Helmholz free energy is

$$\dot{\psi}_1 = -\dot{\theta} C_1 \ln\theta + K_1 \dot{\rho}_1 \tag{85}$$

and

$$\dot{\psi}_2 = -\dot{\theta} C_2 \ln\theta + K_2 \dot{\rho}_2 \tag{86}$$

where (27), (80), and (82) is used.

To show that the problem is complex even though the constitutive assumptions are quite simple in structure, the terms needed in the energy equation will be written down. The reduced energy equation (51) together with (53) may be written as

$$\begin{aligned} 0 \;=\; & \theta \sum_{a=1}^{\Re} \dot{\rho}_a \eta_a + \theta \sum_{a=1}^{\Re} (\rho_a \dot{\eta}_a) + \operatorname{div} \sum_{a=1}^{\Re} \mathbf{q}_a \\ & + \sum_{a=1}^{\Re} \rho_a \dot{\psi}_a + \sum_{a=1}^{\Re} \hat{c}_a \psi_a + \dot{\theta} \sum_{a=1}^{\Re} \rho_a \eta_a \end{aligned} \tag{87}$$

The first term in (87) is the expression

$$\begin{aligned} \theta \sum_{a=1}^{2} \dot{\rho}_a \eta_a \;=\; & \theta \dot{\rho}_1 \left(-\frac{\partial \psi_1}{\partial \theta} - R_1 \frac{\partial \psi_1}{\partial \rho_1} - \frac{R_1}{\rho_1} \psi_1 \right) \\ & + \theta \dot{\rho}_2 \left(-\frac{\partial \psi_2}{\partial \theta} + R_1 \frac{\partial \psi_2}{\partial \rho_2} + \frac{R_1}{\rho_2} \psi_2 \right) \end{aligned} \tag{88}$$

i.e.

$$\begin{aligned} \theta \sum_{a=1}^{2} \dot{\rho}_a \eta_a \;=\; & \theta \dot{\rho}_1 \left(C_1 \ln\theta - R_1 K_1 \right) \\ & + \theta \dot{\rho}_1 \left(-\frac{R_1}{\rho_1} \left(C_1 \theta \left(1 - \ln\theta \right) + K_1 \rho_1 + L_{12} \right) \right) \\ & + \theta \dot{\rho}_2 \left(C_2 \ln\theta + R_1 K_2 \right) \\ & + \theta \dot{\rho}_2 \left(\frac{R_1}{\rho_2} \left(C_2 \theta \left(1 - \ln\theta \right) + K_2 \rho_2 \right) \right) \end{aligned} \tag{89}$$

The second term is

$$\theta \sum_{a=1}^{2} (\rho_a \dot{\eta}_a) \;=\; \theta \rho_1 \left(\frac{C_1}{\theta} \dot{\theta} + \frac{R_1}{\rho_1^2} \left(C_1 \theta \left(1 - \ln\theta \right) + K_1 \rho_1 + L_{12} \right) \right)$$

$$
\begin{aligned}
&+\theta\rho_1\left(\frac{R_1C_1}{\rho_1}\ln\theta-\frac{R_1}{\rho_1}K_1\right)\\
&+\theta\rho_2\left(\frac{C_2}{\theta}\dot{\theta}-\frac{R_1}{\rho_2^2}\left(C_2\theta\left(1-\ln\theta\right)+K_2\rho_2\right)\right)\\
&+\theta\rho_2\left(-\frac{R_1C_2}{\rho_2}\ln\theta+\frac{R_1}{\rho_2}K_2\right)
\end{aligned}
\tag{90}
$$

The third term is given by the constitutive assumptions (46) and (47). The fourth term in (87) is

$$
\sum_{a=1}^{2}\rho_a\dot{\psi}_a=\rho_1\left(-\dot{\theta}C_1\ln\theta+K_1\dot{\rho}_1\right)+\rho_2\left(-\dot{\theta}C_2\ln\theta+K_2\dot{\rho}_2\right) \tag{91}
$$

The fifth term is

$$
\begin{aligned}
\sum_{a=1}^{2}\hat{c}_a\psi_a &= \sum_{a=1}^{\Re}\dot{\rho}_a\psi_a=\dot{\rho}_1\left(C_1\theta\left(1-\ln\theta\right)+K_1\rho_1+L_{12}\right)\\
&\quad+\dot{\rho}_2\left(C_2\theta\left(1-\ln\theta\right)+K_2\rho_2\right)
\end{aligned}
\tag{92}
$$

and the last term is

$$
\begin{aligned}
\dot{\theta}\sum_{a=1}^{2}\rho_a\eta_a &= \dot{\theta}\rho_1\left(-\frac{\partial\psi_1}{\partial\theta}-R_1\frac{\partial\psi_1}{\partial\rho_1}-\frac{R_1}{\rho_1}\psi_1\right)\\
&\quad+\dot{\theta}\rho_2\left(-\frac{\partial\psi_2}{\partial\theta}+R_1\frac{\partial\psi_2}{\partial\rho_2}+\frac{R_1}{\rho_2}\psi_2\right)
\end{aligned}
\tag{93}
$$

i.e.

$$
\begin{aligned}
\dot{\theta}\sum_{a=1}^{2}\rho_a\eta_a &= \dot{\theta}\rho_1\left(C_1\ln\theta-R_1K_1\right)\\
&\quad+\dot{\theta}\rho_1\left(-\frac{R_1}{\rho_1}\left(C_1\theta\left(1-\ln\theta\right)+K_1\rho_1+L_{12}\right)\right)\\
&\quad+\dot{\theta}\rho_2\left(C_2\ln\theta+R_1K_2\right)\\
&\quad+\dot{\theta}\rho_2\left(\frac{R_1}{\rho_2}\left(C_2\theta\left(1-\ln\theta\right)+K_2\rho_2\right)\right)
\end{aligned}
\tag{94}
$$

Some of the terms in (89)-(94) are canceled out, but the matter is still complicated. Indeed, the equation system closed, since the eleven unknown

properties are given by the following introduced equations: (31) and (32) (mass balance), (31) (energy balance), (74) and (75) (thermodynamic laws), (70) (constitutive relation for the reaction kinetics) together with (33) (restriction), (46) and (47) (constitutive relations for the heat flux), and (78) and (79) (constitutive relations for the Helmholz free energy).

The two discussed models include the following material constants: C_1, C_2, K_1, K_2, L_{12}, and R_1 (or G_{12}). This can be compared to the number of material constants introduced in the Stefan's problem which does not include any constants related to the reaction kinetics.

The strategy discussed in this Section as a possible way to obtain equations describing the temperature field and the mass concentration field for the constituents at different times, can be extended, and cases where more than two constituents are considered can be studied. One example is the case of freezing pore water containing chlorides. In order to obtain equations for the temperature field and the mass concentration field of ice, liquid water and chlorides, a more detailed study of the reaction kinetics and the description of the Helmholz free energy for the individual constituents, must be done. Another important thermodynamic problem to be solved is cases, where phase changes occur and where the constituents are also allowed to have a motion, i.e. when $\mathbf{x}'_a(\mathbf{x}, t) \neq \mathbf{0}$. In the presentation given in this Section, the motion was assumed to be restricted (i.e. $\mathbf{x}'_a(\mathbf{x}, t) = \mathbf{0}$). The (global) motion of liquid water during the freezing of pore water may, however, play an important rule when, for example, the damages of concrete at low temperatures are studied.