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Towards a continuum thermodynamics framework for mechanism based modelling of oxidative ageing in bitumen

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ABSTRACT

A reaction-diffusion framework for modelling oxidative ageing in bitumen is derived from thermodynamics of irreversible processes (TIP). The link between continuum scale and molecular level is established through an activity model based on solubilities and molar volumes. General features are demonstrated exemplary for the so-called “spurt oxidation process”. Key aspects of the corresponding model are discussed by means of film ageing simulations.

KEYWORDS

Bitumen; oxidative aging; reaction-diffusion model; continuum thermodynamics; non-equilibrium thermodynamics

1. Introduction

Due to its impact on the performance of asphalt pavements, oxidative ageing of bitumen is the subject of intensive experimental research already for various decades. Not only the complexity of bitumen as such makes a sound understanding of this process extremely difficult. Oxidation processes at molecular level effects bitumen’s microstructure, i.e. the structural arrangement of molecules, which in turn leads to changes in rheological properties. Hence, oxidative ageing of bitumen is a complex multi-scale / multi-physics problem.

Information about oxidative ageing is typically obtained from dark film ageing in combination with infrared spectrometry and rheometry, see, e.g., Petersen (2009), Tarsi et al. (2018), Feng et al. (2016) and Hofko et al. (2018) as well as papers cited therein. These experiments identify sulfoxides and carbonyl groups as the main reaction products of the oxidation process. Furthermore, the increase in sulfoxides and carbonyl groups correlates usually well with the observed hardening of bitumen. It should be noted, however, that for bitumen exposed to air-blowing at 260°C, no changes in the infrared spectrum could be observed in Soenen et al. (2016), despite the increase in viscosity. This indicates exemplary, that different conditions may activate different mechanisms.

Since, bitumen consists of a large number of complex molecular compounds, classification of bitumen by detailed separation into elementary constituents is hardly feasible. Therefore, a classification scheme based on solubility in terms of so-called SARA fractions (saturates, aromatics / naphthenics, resins and asphaltenes) is usually preferred. For an overview, see, e.g.,

Read and Whiteoak (2003) or Branthaver and Huang (2015). A modification of the procedure described in the ASTM standard ASTM (2001), allowing for a more detailed separation, is proposed in Handle et al. (2016).

Modelling is an essential part of the process of gaining insight and understanding. Existing models for oxidative ageing can be classified according to the adopted perspective. Here, we distinguish between molecular perspective, microstructural perspective and rheological perspective to be discussed individually in more detail below.

The process of formulating and testing hypotheses about the oxidation mechanisms at molecular level is going on already for at least 50 years, Martin (1966). A partial overview about this topic can be found in Xin (2012). Initially, oxidative ageing was believed to be a free-radical chain mechanism. However, studies using different antioxidants could not really confirm this hypothesis, King (1993). From observing, that reaction rate is not changed by adding free radical initiators, it is concluded in van Gooswilligen et al. (1985) that the oxidation mechanism cannot be a conventional free radical chain reaction. A catalyzed oxycyclic mechanism based on electron transfer mechanisms is proposed in King (1993). An inhibited autoxidation mechanism is suggested in Herrington (2004). Furthermore, a number of experimental results indicate the existence of at least two chemical processes: a fast “spurt” process and a much slower “long term” process. Spectroscopy results suggest in addition, that the spurt process produces mostly sulfoxides, whereas the slow “long term” process generates primarily sulfoxides and carbonyl groups, but at slower rate. Peterson and co-workers discuss in a number of papers possible chemical mechanisms for these processes, see, e.g., Petersen (2009), Petersen and Harnsberger (1998) and Petersen and Glaser (2011).

The microstructural perspective relates changes in bitumen’s micro-structure due to oxidative ageing with changes in rheological properties. This requires a hypothesis about the structural arrangement of molecules or SARA fractions of different type. Regarding the latter, two main approaches exist, the colloidal hypothesis Read and Whiteoak (2003) and the dispersed polar fluid hypothesis Jones and Kennedy (1991). For a more detailed discussion, see Cebon and Cheung (2015) and papers cited therein. It should be noted, that the validity of these hypotheses is still subjected to controversial debates, see, e.g., Lesueur (2009a) and Redelius (2006).

The model proposed, for instance, in Eberhardsteiner et al. (2014) employs a variant of the colloidal hypothesis. Furthermore, it assumes, that oxidative ageing causes an increase in apparent asphaltene content accompanied by the evolution of an interaction phase. Given the apparent asphaltene content, the rheological properties of the bitumen are deduced based on a micromechanical approach in combination with a homogenization procedure. However, reaction kinetics and re-organization kinetics are only indirectly represented by means of an increase in apparent asphaltene content and an empirical relation between apparent asphaltene content and the volume of an interaction phase.

Models developed from a rheological perspective depart from phenomenological diffusion-reaction models. Reaction kinetics as well as changes in rheological properties and diffusivity are captured by empirical relations based on experimental results and prevailing hypotheses developed from a molecular perspective. A first attempt in this direction was undertaken already in 1954 by Van Oort (1954). Furthermore, a model which intends to mimic not only the diffusion of oxygen into the system but, in addition, the out-diffusion of lighter fractions, is used by Terrenzio et al. (1997). Models accounting for a dual reaction mechanism have been developed, for instance, by Glover et al. (2008), Han (2011) and Herrington (2012). All these models are rather phenomenological in the sense that they do not include explicit information about bitumen composition other than, for instance, sulphur content. Furthermore, the interplay between oxidation at molecular level, structural changes and changes in diffusivity and

$\mathbf{v}$	reference velocity
ρ_α	partial density of species α
M_α	molecular mass of one representative of species α , $[M_\alpha] = \frac{\text{g}}{\text{mol}}$
χ_α	molar fraction, $\chi_\alpha = \frac{n_\alpha}{n_{\text{tot}}} = \frac{\text{number of molecules of species } \alpha}{\text{total number of molecules}}$
m_α	mass of species α , $m_\alpha = M_\alpha \chi_\alpha$
c_α	molar concentration, $c_\alpha = \frac{\rho_\alpha}{M_\alpha}$, $[c_\alpha] = \frac{\text{mol}}{\text{cm}^3}$
w_α	mass concentration, $w_\alpha = \frac{\rho_\alpha}{\rho}$
r_α	source / sink term
s_α	stoichiometric coefficient
a_α	activity
γ_α	activity coefficient
Λ	reaction rate density
R	gas constant, $R = 8.3144598 \cdot 10^7 \frac{\text{g cm}^2}{\text{s}^2 \text{K mol}}$
$(\cdot)_{,j}$	partial derivative with respect to the spatial coordinate x_j , $(\cdot)_{,j} = \frac{\partial}{\partial x_j}(\cdot)$
$\text{div} \mathbf{u}$	divergence of a vector $\mathbf{u}$
c_1^s	oxygen concentration at free surface, $c_1^s = 8.1 \cdot 10^{-7} \frac{\text{mol}}{\text{cm}^3}$ taken from Herrington (2012)

Table 1. List of selected symbols.

rheological properties remains hidden in purely phenomenological parameters. On the other hand, for a practically feasible characterization of the ageing behaviour of different bitumens, these models are rather advantageous.

The different perspectives discussed above either capture only certain parts of the process or, their usability for gaining deeper insight is limited due to the rather phenomenological character of the corresponding models. Development of more comprehensive models requires significant conceptual effort in the near future.

Here, a first attempt is made by proposing a mechanism based reaction-diffusion framework, suitable for hypothesis testing, in particular hypotheses regarding oxidation mechanisms at molecular scale. This requires to connect molecular level and continuum scale. Continuum thermodynamics of mixtures provides a way of doing this. For instance, diffusion equations derived within the frame of continuum thermodynamics do not rely on the gradient in concentration of the diffusing species but, on the gradient in differences in chemical potentials. The chemical potential of a species in a mixture contains an activity coefficient in order to express the deviation from the chemical potential of the pure substance. Activity models, on the other hand, can be formulated by means of solubilities, molar volumes, etc., of all species in the mixture, which establishes a link between molecular level and continuum scale by means of physically meaningful concepts. This is demonstrated exemplary using the mechanism proposed by Petersen (2009) for the so-called “spurt oxidation”.

2. Continuum thermodynamics framework

The reaction-diffusion model presented here, is derived in the framework of thermodynamics of irreversible processes (TIP), see, e.g., Mueller and Ruggeri (2013). Table 1 summarises the employed notation. We consider a continuous mixture of N individual species occupying at

time τ a region $\mathcal{B}$ in space with boundary $\partial\mathcal{B}$. The local mass balance for species α , valid everywhere in $\mathcal{B}$, is given by

$$\partial_\tau \rho_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) = r_\alpha \quad (1)$$

with partial density ρ_α and diffusion flux vector $\mathbf{J}_\alpha = J_{\alpha 1} \mathbf{e}_1 + J_{\alpha 2} \mathbf{e}_2 + J_{\alpha 3} \mathbf{e}_3$, where the base vectors of a Cartesian coordinate system are denoted by $\mathbf{e}_k, k = 1, 2, 3$. The specific choice for the reference velocity $\mathbf{v}$ is partially a matter of taste but depends on the other hand also on the characteristics of the problem. Production or consumption of species α , e.g., due to chemical reactions, is accounted for by source / sink terms r_α , and ∂_τ indicates the partial derivative with respect to time τ .

TIP relies on the assumption that tensorial quantities depend linearly on the gradients of corresponding conjugate quantities. The conjugate quantities of the mass fluxes are respective differences in chemical potentials μ_β . Therefore, the components of the individual flux vectors are given by

$$J_{\alpha j} = -\frac{1}{T} \sum_{\beta=1}^{N-1} L_{\alpha\beta} [\mu_\beta - \mu_N]_{,j} \quad (2)$$

with absolute temperature T and purely phenomenological coefficients $L_{\alpha\beta}$. The partial derivative of a quantity Q with respect to the spatial coordinate x_j is indicated by $Q_{,j}$.

Provided that there is only one chemical reaction, the individual source / sink terms r_α posses the following general form

$$r_\alpha = \Lambda s_\alpha M_\alpha \quad (3)$$

with reaction rate density Λ , stoichiometric coefficients s_α and the molar masses of individual representatives of species α , M_α .

Regarding the chemical potentials of the individual species, we use a standard approach

$$\mu_\alpha = \mu_\alpha^0 + \ln a_\alpha = \mu_\alpha^0 + \ln \chi_\alpha + \ln \gamma_\alpha \quad (4)$$

where μ_α^0 is the chemical potential of the pure species and the activities a_α account for the deviation from μ_α^0 in the case of a mixture. The activity of species α is supposed to be proportional to its molar fraction in the mixture, i.e., $a_\alpha = \gamma_\alpha \chi_\alpha$ with activity coefficient γ_α .

It is worth noting, that the balance of momentum is not taken into account at this stage. Furthermore, the absence of terms related to heat conduction indicates that we are limiting ourself at the moment to isothermal conditions.

As already mentioned above, only one chemical reaction is considered here. In this case, the entropy production Π_0 due to this chemical reaction is given by

$$\Pi_0 = \Lambda A \geq 0, \quad (5)$$

with chemical affinity A ,

$$A = - \sum_{\alpha=1}^N \mu_\alpha s_\alpha. \quad (6)$$

The fact, that at equilibrium, affinity and reaction rate density have to vanish simultaneously, will become crucial for specifying in more detail the reaction rate density.

3. Reaction diffusion model for spurt reaction

3.1. Principal design of the model

Classification of bitumen in terms of composition can be accomplished, for instance, by means of so-called SARA fractions, Read and Whiteoak (2003). SARA stands for saturates, aromatics / naphthenics, resins and asphaltenes, which are distinguishable by their solubility in different solvents.

We consider the spurt reaction sketched in Fig. 1. In order to design the most simple possible model, we ignore the intermediate product and the possible generation of free radicals, assuming a simplified reaction path as indicated by a dashed line in Fig. 1. The corresponding reaction can be described as follows. A dioxygen molecule comes close to a saturated ring, situated between two aromatic rings. Two hydrogen atoms are taken off from the saturated ring, which converts the latter into an aromatic ring. This process is called “aromatizing” in the following. In addition, the O_2 and the two hydrogen atoms find somewhere else a sulfur atom. A sulfoxide is formed and the remaining oxygen forms together with the two hydrogen atoms a water molecule.

Since the mechanism requires the existence of saturated rings close to aromatic ones, only aromatics / naphthenics, resins and asphaltenes (ARA) can be affected by such a reaction, whereas saturates do not participate at all. In view of the previous section and the envisaged reaction mechanism, we define the following five species

- (1) O_2
- (2) H_2O
- (3) aromatized compounds (ARA*) with one sulfoxide in each compound
- (4) aromatizable compounds, which means aromatics, resins and asphaltenes with traces of sulfur (ARA)
- (5) saturates

numbered by $\alpha = 1, \dots, 5$.

We assume that every ARA member can be affected only once, which implies that the ARA species consists of average compounds. Furthermore, the simplified chemical reaction equation for short term oxidation reads

which corresponds to the following set of stoichiometric coefficients

$$s_1 = s_4 = -1, s_3 = s_2 = 1, s_5 = 0. \quad (7)$$

The characteristics of the reaction imply certain relations between individual molar fractions. Since, in addition, the sum of individual molar fractions equals one, all molar fractions can

Figure 1. Spurt reaction as proposed in Petersen and Glaser (2011). “ASP” indicates moities with strongly associating components, whereas “R” stands for moities with weakly associating components. Free radicals means $\text{RO}\cdot$, $\text{OH}\cdot$, etc. The dashed line indicates the simplified reaction path assumed here.

be expressed by means of χ_1 , χ_2 and the initial molar fractions of saturates, χ_5^0 , as follows

$$\chi_3 = \chi_2, \quad (8)$$

$$\chi_5 = \chi_5^0[1 - \chi_1 - \chi_2], \quad (9)$$

$$\chi_4 = [1 - \chi_5^0][1 - \chi_1 - \chi_2] - \chi_2. \quad (10)$$

3.2. Mass balances

For the system considered here, dioxygen is the only species which actually diffuses. All other species remain, on average, at their spatial locations. Therefore, $\mathbf{v} = \mathbf{0}$ is the natural choice here. In order to ensure direct comparability with related contributions in the literature, the mass balances are rewritten in molar concentrations. The essential mass balances in our model read therefore

$$\partial_\tau c_1 + \text{div} \bar{\mathbf{J}}_1 = \bar{r}_1 = -\Lambda \quad (11)$$

$$\partial_\tau c_2 = \bar{r}_2 = \Lambda \quad (12)$$

with $\bar{\mathbf{J}}_1 = \frac{1}{M_1} \mathbf{J}_1$, $\bar{r}_1 = \frac{1}{M_1} r_1$ and $\bar{r}_2 = \frac{1}{M_2} r_2$.

For deriving explicitly diffusion flux and reaction rate density we prefer, however, to work with molar fractions. The formulas for conversion between molar fractions and molar concentrations are given in appendix A.

3.3. Regular solution type activity model

The activity model discussed in Vidal (2003) in the context of regular solution theory reads

$$\ln \gamma_\alpha = \frac{v_\alpha^*}{RT} [\delta_\alpha - \bar{\delta}]^2 \quad (13)$$

with

$$\bar{\delta} = \sum_{\alpha=1}^N \delta_{\alpha} \Phi_{\alpha} \quad (14)$$

where v_{α}^* is the molar volume of the pure k-th substance in liquid state and, δ_{α} is the solubility parameter of the k-th substance. Furthermore, Φ_{α} is the corresponding volumetric fraction. For an ideal gas, volumetric fraction and molar fraction are identical. Here, however, such a simple relation cannot be expected. Most likely, the Φ_{β} are functions of all molar fractions, temperature and pressure. Here, we use

$$\Phi_{\alpha} = \frac{v_{\alpha}^* \chi_{\alpha}}{\sum_{\beta=1}^N v_{\beta}^* \chi_{\beta}} = \frac{v_{\alpha}^* \chi_{\alpha}}{V^*}. \quad (15)$$

3.4. Diffusion part

Since dioxygen is the only species which diffuses, (2) reads in matrix notation

$$\begin{pmatrix} J_{1j} \\ J_{2j} \\ J_{3j} \\ J_{4j} \\ J_{5j} \end{pmatrix} = \begin{pmatrix} J_{1j} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = -\frac{1}{T} \begin{pmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \\ L_{51} & L_{52} & L_{53} & L_{54} \end{pmatrix} \cdot \begin{pmatrix} [\mu_1 - \mu_5]_{,j} \\ [\mu_2 - \mu_5]_{,j} \\ [\mu_3 - \mu_5]_{,j} \\ [\mu_4 - \mu_5]_{,j} \end{pmatrix}$$

and the last four equations can be used to express all gradients in chemical potential differences by means of one particular gradient in chemical potential difference, for instance $[\mu_1 - \mu_5]_{,j}$

$$\begin{aligned} [\mu_2 - \mu_5]_{,j} &= \beta_1 [\mu_1 - \mu_5]_{,j} \\ [\mu_3 - \mu_5]_{,j} &= \beta_2 [\mu_1 - \mu_5]_{,j} \\ [\mu_4 - \mu_5]_{,j} &= \beta_3 [\mu_1 - \mu_5]_{,j} \end{aligned}$$

where the β_i are functions of all the L_{ij} for which $i \geq 2$. Eventually, all coefficients can be condensed in one single parameter L_{11}^*

$$J_{1j} = -\frac{L_{11}^*}{T} [\mu_1 - \mu_5]_{,j}$$

and by using the definition of the chemical potentials, we obtain

$$J_{1j} = -L \left\{ \left[1 + \frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_1} \right] \chi_{1,j} + \left[\frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_2} \right] \chi_{2,j} \right\} \quad (16)$$

if in addition the concept of mobility is used ($L = \frac{RL_{11}^*}{\chi_1}$). Furthermore, it follows from (13), that

$$A_{15} = \ln \frac{\gamma_1}{\gamma_5} = \frac{v_1^* [\delta_1 - \bar{\delta}]^2}{v_5^* [\delta_5 - \bar{\delta}]^2}. \quad (17)$$

In order to compute the required derivatives, we by apply chain rule, which gives

$$\frac{\partial A_{15}}{\partial \chi_1} = \frac{\partial A_{15}}{\partial \bar{\delta}} \frac{\partial \bar{\delta}}{\partial \chi_1} \qquad \frac{\partial A_{15}}{\partial \chi_2} = \frac{\partial A_{15}}{\partial \bar{\delta}} \frac{\partial \bar{\delta}}{\partial \chi_2} \quad (18)$$

with

$$\frac{\partial A_{15}}{\partial \bar{\delta}} = 2 \frac{v_1^*}{v_5^*} \frac{[\delta_1 - \bar{\delta}][\delta_1 - \delta_5]}{[\delta_5 - \bar{\delta}]^3} . \quad (19)$$

and, taking into account (15),

$$\frac{\partial \bar{\delta}}{\partial \chi_1} = \frac{v_1^*}{V^*} [d_1 - \bar{\delta}] \quad , \qquad \frac{\partial \bar{\delta}}{\partial \chi_2} = \frac{v_2^*}{V^*} [d_2 - \bar{\delta}] . \quad (20)$$

Hence, the components of the diffusion flux vector are completely determined by means of one purely phenomenological coefficient, solubilities, molar volumes, molar fractions of dioxygen and water and their spatial gradients.

3.5. Reaction part

In order to relate the reaction rate density as well to information about composition, a reaction model following Pekar M. and Samohyl I. (2014) is proposed here.

The reaction rate density is approximated by the following second order polynomial in activities

$$\begin{aligned} \Lambda \approx P_\Lambda = B_0 &+ \frac{1}{2} B_{11} a_1^2 + B_{12} a_1 a_2 + B_{13} a_1 a_3 + B_{14} a_1 a_4 + B_{15} a_1 a_5 \\ &+ \frac{1}{2} B_{22} a_2^2 + B_{23} a_2 a_3 + B_{24} a_2 a_4 + B_{25} a_2 a_5 \\ &+ \frac{1}{2} B_{33} a_3^2 + B_{34} a_3 a_4 + B_{35} a_3 a_5 \\ &+ \frac{1}{2} B_{44} a_4^2 + B_{45} a_4 a_5 \\ &+ \frac{1}{2} B_{55} a_5^2 \end{aligned} \quad (21)$$

which only takes into account binary interactions in order to keep the number of parameters as small as possible. In what follows, the aim is to specify the coefficients in P_Λ .

Indicating equilibrium quantities by a superscript $\ominus$, using (6) together with (4) and taking into account (7), the condition of vanishing affinity at equilibrium eventually reads

$$\ln \left(\frac{a_1^\ominus a_4^\ominus}{a_2^\ominus a_3^\ominus} \right) = \frac{\mu_A^\ominus}{RT} \quad (22)$$

with $\mu_A^\ominus = \mu_1^\ominus + \mu_4^\ominus - \mu_2^\ominus - \mu_3^\ominus$, which enables us to define an equilibrium constant K

$$K = \frac{a_1^\ominus a_4^\ominus}{a_2^\ominus a_3^\ominus} . \quad (23)$$

species	density $\frac{\text{g}}{\text{cm}^3}$	molecular weight $\frac{\text{g}}{\text{mol}}$	molar volume $\frac{\text{cm}^3}{\text{mol}}$	solubility	
				$\sqrt{\text{MPa}}$	$\sqrt{\frac{\text{g}}{\text{cm s}^2}}$
oxygen	1.114	32	28.0	14.0	44272.2
water	0.988	18	18.2	48.0	151790.4
ARA*			1709.0	20.0	63246.0
ARA aromatics	1.006	440	437.0	21.0	
resins	1.054	990	940.0	19.0	
asphaltenes	1.200	4500	3750.0	20.0	
average			1709.0	20.0	63246.0
saturates	0.887	370	417.0	16.5	52177.9

Table 2. Parameters used in simulations. The density for oxygen refers to liquid oxygen. The conversion factor for solubilities is $1\sqrt{\text{MPa}} = 3162.3\sqrt{\frac{\text{g}}{\text{cm s}^2}}$

The general expression for the reaction rate density has to be valid in equilibrium and in non-equilibrium situations. At equilibrium, the activities take their equilibrium values, i.e., $\Lambda^\ominus = \Lambda(a_\alpha = a_\alpha^\ominus)$. In addition,

$$B_{14}a_1^\ominus a_4^\ominus + B_{23}a_2^\ominus a_3^\ominus = [B_{14} + \frac{1}{K}B_{23}]a_1^\ominus a_4^\ominus \quad (24)$$

due to (23). After modifying $\Lambda^\ominus$ according to (24), $\Lambda^\ominus = 0$ can be achieved by setting all coefficients related to terms 1 and $a_\alpha^\ominus a_\beta^\ominus$, respectively, equal to zero. This yields

$$B_0 = 0, \quad B_{23} = -KB_{14} \quad \text{and} \quad B_{ij} = 0 \quad \text{if} \quad i \neq 1, 2 \quad \text{and} \quad j \neq 3, 4. \quad (25)$$

Therefore, the reaction rate density (21) reduces to

$$\Lambda = B_{14}[a_1 a_4 - K a_2 a_3]. \quad (26)$$

From the general definition of the activities together with the activity coefficients given by the regular solution model (13), we obtain

$$a_\alpha = \chi_\alpha \exp\left(\frac{v_\alpha^*}{RT} [\delta_\alpha - \bar{\delta}]^2\right) \quad (27)$$

and

$$\Lambda = B_{14} \left[\chi_1 \chi_4 \exp\left(\frac{v_1^*}{RT} [\delta_1 - \bar{\delta}]^2 + \frac{v_4^*}{RT} [\delta_4 - \bar{\delta}]^2\right) \right. \quad (28)$$

$$\left. - \chi_2 \chi_3 \exp\left(\frac{v_2^*}{RT} [\delta_2 - \bar{\delta}]^2 + \frac{v_3^*}{RT} [\delta_3 - \bar{\delta}]^2\right) K \right] \quad (29)$$

A closer look reveals, that the first term in brackets corresponds to the forward reaction, whereas the second term encodes the backward reaction. The forward reaction is possible as long as dioxygen and aromatizable compounds are available, whereas the backward reaction requires the presence of water and aromatized compounds. Since we assume, that the oxidation process is irreversible, K must be small enough in order for the second term in the brackets

Figure 2. R_{j_1} (left) and R_{j_2} (right) as functions of χ_2 , evaluated for two different amounts of dioxygen, $\chi_1^* = 0.001$ (solid lines) and $\chi_1^* = 0.15$ (dashed lines) and three different compositions given in Sec. 4.1, where increasing χ_5^0 is indicated by increasing line thickness. The range of χ_2 is computed by means of (39).

to be negligible regardless the value of $\chi_2\chi_3$. Therefore, the result for the reaction rate reads

$$\Lambda = B_{14}\chi_1\chi_4 \exp\left(\frac{v_1^*}{RT} [\delta_1 - \bar{\delta}]^2 + \frac{v_4^*}{RT} [\delta_4 - \bar{\delta}]^2\right) \quad (30)$$

or

$$\Lambda = B_{14}\chi_1 \left[[1 - \chi_5^0][1 - \chi_1 - \chi_2] - \chi_2\right] \exp\left(\frac{v_1^*}{RT} [\delta_1 - \bar{\delta}]^2 + \frac{v_4^*}{RT} [\delta_4 - \bar{\delta}]^2\right) \quad (31)$$

if (9) is taken into account.

4. Results

4.1. Material parameters used in this section

The material parameters used in the following are given in Table 2. Data for SARA-fractions are taken from Powers (2014) and Akbarzadeh et al. (2005), respectively. Data for water and dioxygen originate from standard tables. Here, we choose values according to the CGS-system (centimeter-gram-second).

The model is able to distinguish between compositions by means of saturate content χ_5^0 . Three different values for χ_5^0 are considered: $\chi_5^0 = 0.15, 0.25, 0.35$ referred to as composition 1, 2 and 3, respectively, in the following.

4.2. Direct inspection of flux terms and reaction rate density

The reaction rate density (30) normalized by B_{14} can be evaluated directly for a material point as a function of χ_1 and χ_2 . This is also possible for individual terms of the diffusion flux (16) by considering

$$-\frac{J_{1j}}{L} = j_1\chi_{1,j} + j_2\chi_{2,j} \quad (32)$$

Figure 3. Reaction rate density normalized by B_{14} as function of the molar fractions of oxygen χ_1 , and water χ_2 for $\chi_5^0 = 0.35$. The range of χ_1 , χ_2 has been chosen beyond realistic values in order to illustrate trends.

and evaluating the terms

$$j_1 = 1 + \frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_1} \quad (33)$$

$$j_2 = \frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_2} \quad (34)$$

separately. Evaluation of $\frac{\Lambda}{B_{14}}$, j_1 and j_2 is performed by using the computer algebra system Maple.

Of particular interest is the question, how $\frac{\Lambda}{B_{14}}$, j_1 and j_2 are affected by the history experienced by a considered material point in terms of chemical reaction, i.e., its “ageing” state. However, keeping the amount of dioxygen fixed and varying the “ageing” state, requires some preliminary considerations.

A material point corresponds to a system of n_{tot} molecules. For a material point which did not undergo any ageing process yet, we have $n_2 = 0, n_3 = 0, n_4 = n_4^0$ and $n_5 = n_5^0$. In addition, we assume the presence of a fixed amount n_1^* of dioxygen molecules, hence

$$n_{\text{tot}}^0 = n_1^* + n_4^0 + n_5^0. \quad (35)$$

On the other hand, ageing history is reflected by the number of water molecules n_2 . For a material point corresponding to a system with the same amount of dioxygen, but having experienced already a certain reaction history,

$$n_{\text{tot}} = n_1^* + n_2 + n_2 + [n_4^0 - n_2] + n_5^0 = n_{\text{tot}}^0 + n_2 \quad (36)$$

holds, due to the stoichiometry of the reaction. Defining

$$\chi_1^* = \frac{n_1^*}{n_{\text{tot}}^0} \quad (37)$$

Figure 4. Reaction rate density normalized by B_{14} as function of χ_2 for fixed dioxygen content, $\chi_1^* = 0.001$ (left) and $\chi_1^* = 0.15$ (right) and three different compositions, i.e., three different values for χ_5^0 , see Sec. 4.1. The range of χ_2 has been chosen beyond realistic values in order to illustrate trends.

we obtain after elementary computations

$$\chi_1 = \hat{\chi}_1(\chi_1^*, \chi_2) = \chi_1^*[1 - \chi_2], \quad (38)$$

which establishes a relation between χ_1 and χ_2 for the case, that the number of dioxygen molecules is kept constant and the “ageing” stage is varied. Furthermore, we are interested in the maximum value for χ_2 . The value for n_2 is limited by number of reactants, n_4^0 . Therefore,

$$\chi_{2,\max} = \frac{[1 - \chi_1^*][1 - \chi_5^0]}{1 + [1 - \chi_1^*][1 - \chi_5^0]} \quad (39)$$

holds.

Evaluating the term

$$q(\chi_1, \chi_2) := \frac{\chi_1}{1 - \chi_1 - \chi_2} \quad (40)$$

contained in both j_1 and j_2 , see (33) and (34), for $\chi_1 = \hat{\chi}_1$, see (38), yields

$$q(\chi_1 = \hat{\chi}_1, \chi_2) = \frac{\chi_1^*}{1 - \chi_1^*} \quad (41)$$

which reveals that $q(\chi_1, \chi_2)$ does not depend at all on reaction history. Since χ_5^0 is not present, it does not depend on composition either. It remains to inspect those terms in j_1 and j_2 related to the derivatives of A_{15} . We define,

$$R_{j_1} = \frac{\chi_1}{q} \frac{\partial A_{15}}{\partial \chi_1} \quad (42)$$

Figure 5. Principal sketch of the cross section a typical film ageing setup and parameters used in the one-dimensional finite element simulations, where l_e is the finite element length, L the phenomenological diffusion parameter, see (16), and Δt_{LB} is the lower limit for the initial time increment to prevent spurious results due to the discontinuous initial conditions applied here at start time, $\tau = 0$. The value for the concentration of dioxygen at the free surface, c_1^s is taken from Herrington (2012).

and

$$R_{j_2} = \frac{\chi_1}{q} \frac{\partial A_{15}}{\partial \chi_2} \quad (43)$$

in order to discuss the influence of the third term in (33) and the second term in (34) on the total results for j_1 and j_2 , respectively. The results for R_{j_1} and R_{j_2} , evaluated for $\chi_1 = \hat{\chi}_1$, as functions of χ_2 are shown in Fig. 2, whereas the results for $L/B14$ are plotted in Figures 3 and 4.

4.3. Film oxidation simulations

A film of thickness $h = 1\text{mm}$ as sketched in Fig. 5 with only one free surface exposed to air is considered. It is assumed here, that a one-dimensional model is sufficient for reproducing the situation along a path in the center, indicated in Fig. 5 by the coordinate axis z . Following Herrington (2012), a fixed dioxygen concentration, $c_1^s = 8.10 \times 10^{-7} \frac{\text{mol}}{\text{cm}^3}$ is prescribed at $z = 0$. Furthermore, the flux of c_1 vanishes at $z = h$, whereas the flux terms of c_2 vanish at $z = 0$ and $z = h$.

The finite element scheme for the one-dimensional case has been implemented in FEniCS, Alnaes et al. (2015).

Oxygen uptake is computed during simulations by

$$\mathcal{C}_{O_2}(\tau) = \frac{1}{h} \int_0^h c_2(\tau, z) dz. \quad (44)$$

The final value of $\mathcal{C}_{O_2}$, $\mathcal{C}_{O_2}^\infty = \mathcal{C}_{O_2}(\tau \rightarrow \infty)$, however, can be determined analytically, since for the steady state, $c_1 = c_1^s$ holds everywhere in the specimen, and, in addition, all reactants are consumed, i.e., $\chi_4(\tau \rightarrow \infty) = 0$. Based on this two conditions and using the conversion formulas given in appendix A

$$\mathcal{C}_{O_2}^\infty = \frac{[1 - \chi_5^0][c_1^s b_1 - c_1^s b_2 + \rho]}{\chi_5^0[b_1 - b_3] + b_3 - 2b_1} \quad (45)$$

is obtained, where the coefficients b_k can be found in appendix A. Because c_1^s is very small

Figure 6. Oxygen uptake in $\frac{\text{mol}}{\text{L}}$ measured by integrating c_2 over film thickness as a function of time in hours for two combinations of diffusion and reaction parameters.

compared with all other values, we use the approximation

$$C_{O_2}^\infty \approx \frac{[1 - \chi_5^0]\rho}{\chi_5^0[b_1 - b_3] + b_3 - 2b_1} \quad (46)$$

in the following. For compositions 1,2 and 3 ($\chi_5^0 = 0.15, 0.25, 0.35$), $C_{O_2}^\infty$ takes the values 0.485, 0.472, 0.456.

Provided that material parameters as listed in Table 2 are known and fixed, the velocity of the process is determined by the two purely phenomenological parameters L and B_{14} , where L determines the diffusion velocity and B_{14} controls directly the reaction speed. The effect of L and B_{14} on process velocity is shown exemplary for two particular combinations of these parameters in Fig 6.

5. Discussion

The model proposed here provides consistent results. Firstly, the reaction rate density Λ (31) vanishes in the absence of reactants, dioxygen ($\chi_1 = 0$) or ARA ($\chi_4 = 0$). Secondly, Λ decreases with progressing oxidation (ageing) as indicated in Fig. 4. Furthermore, final oxygen uptake decreases with increasing amount of saturates, χ_5^0 . Last but not least, the values obtained for final oxygen uptake are of same magnitude as the values reported in Petersen (2009).

In comparison with other reaction-diffusion models, e.g., Herrington (2012), our model possesses the important advantage of having only a small number of purely phenomenological parameters. Equally important, it is able to distinguish between different compositions.

Consequently, in a next step the long term oxidation process described by Petersen (2009) and Petersen and Glaser (2011) should be included in the framework developed here. Since this process is significantly more complex, at least two chemical reactions have to be taken into account.

It should be noted, that diffusion properties are almost not affected by the oxidation process in our model. Fig. 2 shows, that the significant terms of the diffusion flux vector (16), namely $\chi_1 \frac{\partial A_{15}}{\partial \chi_1}$ and $\chi_1 \frac{\partial A_{15}}{\partial \chi_2}$, are of almost no influence on diffusion. It is not to be expected, that

more elaborate activity models, as used for instance in (Akbarzadeh et al., 2005), will change this significantly. The argument used, e.g., by Herrington (2012), that diffusivity depends on viscosity, which in turn depends on ageing, implies, that a change in viscosity cannot be explained either just by accounting for the generation of sulfoxides.

On the other hand, a number of experimental findings indicate, that increase in viscosity cannot be explained just by the formation of carbonyl groups and / or sulfoxides. In Petersen (2009), for instance, it is argued, that the simultaneous changes in polarity and solubility, cause the agglomeration of aromatic compounds, which eventually become part of the asphaltene fraction.

In view of this hypothesis, experimental studies comparing SARA-fractions as well as molecular weight distributions before and after ageing, are of particular interest. Despite the use of bitumens of different origin, different ageing procedures, and partially different chemical analysis methods, transformations in generic fractions, as well an increase in amount of larger molecules or molecular associations is reported in Le Guern et al. (2010); Lu and Isacson (2002); Pauli and Shin-Che (2013); Soenen et al. (2016). Furthermore, Pauli and Shin-Che (2013) link observed structural changes with the increase in viscosity by means of a colloidal model for bitumen proposed by Bullard et al. (2009), see, as well, Lesueur (2009a). It should be noted, however, that the colloidal hypothesis for bitumen is subject of debate, as the discussion in Lesueur (2009b) shows exemplary.

Our model therefore supports the hypothesis, that additional processes occur simultaneously to the formation of sulfoxides and / or carbonyl groups. Therefore, processes related to structure formation, or to the formation of bigger molecules from smaller ones, causing eventually a stiffening of the material must be incorporated in future model development.

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References

- Akbarzadeh, K., Alboudwarej, H., Svrcek, W. Y., and Yarranton, H. W. (2005). A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens. *Fluid Phase Equilibria*, 232(1):159 – 170.
- Alnaes, M., Blechta, J., Hake, J., Johansson, A., Kehlet, B., Logg, A., Richardson, C., Ring, J., Rognes, M., and Wells, G. (2015). The fenics project version 1.5. *Archive of Numerical Software*, 3(100).
- ASTM, D.-. (2001). Standard test methods for separation of asphalt into four fractions. Technical report, ASTM.
- Branthaver, J. and Huang, S.-C. (2015). 2 - analytical separation methods in asphalt research. In Huang, S.-C. and Benedetto, H. D., editors, *Advances in Asphalt Materials*, Woodhead Publishing Series in Civil and Structural Engineering, pages 31 – 57. Woodhead Publishing, Oxford.
- Bullard, J. W., Pauli, A. T., Garboczi, E. J., and Martys, N. S. (2009). A comparison of viscosity-concentration relationships for emulsions. *Journal of Colloid and Interface Science*, 330(1):186–193.
- Cebon, D. and Cheung, C. (2015). 6 - deformation mechanisms of bituminous materials. In Huang,

- S.-C. and Benedetto, H. D., editors, *Advances in Asphalt Materials*, Woodhead Publishing Series in Civil and Structural Engineering, pages 169 – 203. Woodhead Publishing, Oxford.
- Eberhardsteiner, L., Fussl, J., Hofko, B., Handle, F., Hospodka, M., Blab, R., and Grothe, H. (2014). Influence of asphaltene content on mechanical bitumen behavior: experimental investigation and micromechanical modeling. *Materials and Structures*.
- Feng, Z.-G., Bian, H.-J., Li, X.-J., and Yu, J.-Y. (2016). FTIR analysis of uv aging on bitumen and its fractions. *Materials and Structures*, 49(4):1381–1389.
- Glover, C., Martin, A., Chowdhury, A., Han, R., Prapaitrakul, N., Jin, X., and Lawrence, J. (2008). Evaluation of binder aging and its influence in aging of hot mix asphalt concrete: literature review and experimental design. Technical report, Texas Transportation Institute.
- Han, R. (2011). *Improvement to a transport model of asphalt binder oxidation in pavements: Pavement temperature modeling, oxygen diffusivity in asphalt binders and mastics, and pavement air void characterization*. PhD thesis, Texas A&M University.
- Handle, F., Füssl, J., Neudl, S., Grosseegger, D., Eberhardsteiner, L., Hofko, B., Hospodka, M., Blab, R., and Grothe, H. (2016). The bitumen microstructure: a fluorescent approach. *Materials and Structures*, 49(1):167–180.
- Herrington, P. (2004). Effect of concentration on the rate of reaction of asphaltenes with oxygen. *Energy and Fuels*, 18(5):1573–1577. cited By 6.
- Herrington, P. R. (2012). Diffusion and reaction of oxygen in bitumen films. *Fuel*, 94:86 – 92.
- Hofko, B., Porot, L., Falchetto Cannone, A., Poulikakos, L., Huber, L., Lu, X., Mollenhauer, K., and Grothe, H. (2018). Ftir spectral analysis of bituminous binders: reproducibility and impact of ageing temperature. *Materials and Structures*, 51(2):45.
- Jones, D. and Kennedy, T. (1991). THE ASPHALT MODEL: Results of the SHRP Asphalt Research Program. Technical report, University of Texas, Center for Transportation Research.
- King, G. N. (1993). Oxycclics: understanding catalyzed oxidation mechanisms in bitumen and other petroleum products. *Fuel Science and Technology International*, 11(1):201–238.
- Le Guern, M., Chailleux, E., Farcas, F., Dreessen, S., and Mabilie, I. (2010). Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging. *FUEL*, 89(11):3330–3339.
- Lesueur, D. (2009a). The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science*, 145(1):42 – 82.
- Lesueur, D. (2009b). Evidence of the Colloidal Structure of Bitumen. In *Proc. ISAP International Workshop on the Chemo-Mechanics of Bituminous Materials*.
- Lu, X. and Isacson, U. (2002). Effect of ageing on bitumen chemistry and rheology. *Construction and Building Materials*, (16):15–22.
- Martin, K. G. (1966). Influence of stabilisers on bitumen durability. *Journal of Applied Chemistry*, 16(7):197–202.
- Mueller, I. and Ruggeri, T. (2013). *Rational extended thermodynamics*. Springer Tracts in Natural Philosophy. Springer New York.
- Pauli, A. and Shin-Che, H. (2013). Relationship between Asphalt Compatibility, Flow Properties, and Oxidative Aging. *International Journal of Pavement Research and Technology*, 6(1):1–7.
- Pekar M. and Samohyl I. (2014). *The Thermodynamics of Linear Fluids and Fluid Mixtures*. Springer.
- Petersen, J. (2009). A review of the fundamentals of asphalt oxidation. Technical report, Transportation Research Board.
- Petersen, J. C. and Glaser, R. (2011). Asphalt oxidation mechanisms and the role of oxidation products on age hardening revisited. *Road Materials and Pavement Design*, 12(4):795–819.
- Petersen, J. C. and Harnsberger, P. M. (1998). Asphalt aging: Dual oxidation mechanism and its interrelationships with asphalt composition and oxidative age hardening. *TRANSPORTATION RESEARCH RECORD*, (1638):47–55.
- Powers, D. P. (2014). *Characterization and Asphaltene Precipitation Modeling of Native and Reacted Crude Oils*. PhD thesis, University of Calgary.
- Read, J. and Whiteoak, D. (2003). *The Shell Bitumen Handbook*. Thomas Telford Publishing, 5th edition.

- Redelius, P. G. (2006). The structure of asphaltenes in bitumen. *Road Materials and Pavement Design*, 7(sup1):143–162.
- Soenen, H., Xiaohu, L., and Laukkanen, O.-V. (2016). Oxidation of bitumen: molecular characterization and influence on rheological properties. *Rheologica Acta*.
- Tarsi, G., Varveri, A., Lantieri, C., Scarpas, A., and Sangiorgi, C. (2018). Effects of different aging methods on chemical and rheological properties of bitumen. *Journal of Materials in Civil Engineering*, 30(3).
- Terrenzio, L. A., Harrison, J. W., Nester, D. A., and Ming, L. S. (1997). Natural vs. artificial aging. use of diffusion theory to model asphalt and fibreglass-reinforced shingle performance. In *Proceedings of the International Symposium of Roofing Technology*.
- van Gooswilligen, G., de Bats, F. T., and Berger, H. (1985). Oxidation of bitumen in various tests. In *Proceedings of the European Bitumen Conference*, pages 95–101.
- Van Oort, W. P. (1954). *A study of ageing of asphaltic bitumen*. PhD thesis, Technische Hogeschool Delft.
- Vidal, J. (2003). *Thermodynamics*. Editions OPHRYS.
- Williams, T., Kelley, C., and many others (2013). gnuplot 4.6: an interactive plotting program.
- Xin, J. (2012). *Asphalt oxidation kinetics and pavement oxidation modeling*. PhD thesis, Texas A&M University.

Appendix A. Conversion between molar fractions and molar concentrations

Molar fractions χ_α and mass fractions w_α are related by means of

$$c_\alpha = \frac{\rho_\alpha}{M_\alpha} = \frac{\rho_\alpha}{\rho} \frac{\rho}{M_\alpha} = w_\alpha \frac{\rho}{M_\alpha}, \quad (\text{A1})$$

whereas mass fractions w_α are related to molar fractions by

$$w_\alpha = \frac{\rho_\alpha}{\rho} = \frac{\chi_\alpha M_\alpha}{M} \quad \text{with} \quad M = \sum_{\beta} \chi_\beta M_\beta. \quad (\text{A2})$$

Therefore,

$$c_\alpha = \frac{\chi_\alpha}{M} \rho. \quad (\text{A3})$$

from which the following conversion formulas can be obtained

$$\chi_1 = \frac{b_1 c_1}{b_2 c_1 + b_3 c_2 - \rho} \quad \chi_2 = \frac{b_1 c_2}{b_2 c_1 + b_3 c_2 - \rho} \quad (\text{A4})$$

with

$$b_1 = \chi_5^0 [M_4 - M_5] - M_4 \quad (\text{A5})$$

$$b_2 = M_1 - M_4 + \chi_5^0 [M_4 - M_5] \quad (\text{A6})$$

$$b_3 = M_2 + M_3 - 2M_4 + \chi_5^0 [M_4 - M_5] \quad (\text{A7})$$

by taking into account (8) - (10). Molar concentrations can be computed from given molar fractions by

$$c_1 = \frac{\chi_1}{b_2\chi_1 + b_3\chi_2 - b_1} \rho, \quad c_2 = \frac{\chi_2}{b_2\chi_1 + b_3\chi_2 - b_1} \rho. \quad (\text{A8})$$

Furthermore

$$\begin{aligned} \frac{\partial \chi_1}{\partial c_1} &= \frac{b_1[b_3c_2 - \rho]}{[b_2c_1 + b_3c_2 - \rho]^2} & \frac{\partial \chi_1}{\partial c_2} &= -\frac{b_1b_3c_1}{[b_2c_1 + b_3c_2 - \rho]^2} \\ \frac{\partial \chi_2}{\partial c_1} &= -\frac{b_1b_2c_2}{[b_2c_1 + b_3c_2 - \rho]^2} & \frac{\partial \chi_2}{\partial c_2} &= \frac{b_1[b_2c_1 - \rho]}{[b_2c_1 + b_3c_2 - \rho]^2} \end{aligned}$$

are required by the finite element solution scheme. The density of bitumen is about $1.01 - 1.06 \frac{\text{g}}{\text{cm}^3}$.

Appendix B. Finite element implementation

A finite element scheme is used to solve the one-dimensional nonlinear initial boundary value problem. Time discretization of (11) and (12) is performed by means of an implicit Euler method, which yields

$$c_1 + \bar{J}_1' \Delta t - \bar{r}_1 \Delta t - {}^m c_1 = 0 \quad (\text{B1})$$

$$c_2 - \bar{r}_1 \Delta t - {}^m c_2 = 0 \quad (\text{B2})$$

with $\Delta t = t_{m+1} - t_m$, where all quantities refer to time $\tau = t_{m+1}$ except those for which evaluation at $\tau = t_m$ is indicated explicitly by a left super index “ m ”. The weak form of the boundary value problem for the time increment $[t_m, t_{m+1}]$ reads initially

$$\int_0^h [c_1 + \bar{J}_1' \Delta t - \bar{r}_1 \Delta t - {}^m c_1] v \, dz = 0 \quad (\text{B3})$$

$$\int_0^h [c_2 - \bar{r}_1 \Delta t - {}^m c_2] w \, dz = 0 \quad (\text{B4})$$

if the problem is defined on an interval $z \in [0, h]$. Applying integration by parts for the flux term yields

$$\Delta t \int_0^h \bar{J}' v \, dz = \Delta t [\bar{J}_1 v]_0^l - \Delta t \int_0^h \bar{J}_1 v' \, dz \quad (\text{B5})$$

but, since at the boundaries either c_1 is prescribed, which implies that the test function v vanishes, or the flux $\bar{J}_1$ is prescribed to zero, the boundary term in the above equation vanishes

here. Therefore, the weak form reads

$$\begin{aligned} \int_0^h c_1 v \, dz - \int_0^h \bar{J}_1 v' \, dz \, \Delta t - \int_0^h \bar{r}_1 v \, dz \, \Delta t - \int_0^h {}^m c_1 v \, dz &= 0 \\ \int_0^h c_2 w \, dz - \int_0^h \bar{r}_1 w \, dz \, \Delta t - \int_0^h {}^m c_2 w \, dz &= 0 \end{aligned}$$

By adding the above equations, the weak form of the problem can be compiled into one single equation

$$\begin{aligned} \int_0^h c_1 v \, dz - \int_0^h \bar{J}_1 v' \, dz \, \Delta t - \int_0^h \bar{r}_1 v \, dz \, \Delta t + \int_0^h c_2 w \, dz - \int_0^h \bar{r}_2 w \, dz \, \Delta t \\ = + \int_0^h {}^m c_1 v \, dz + \int_0^h {}^m c_2 w \, dz. \end{aligned} \quad (\text{B6})$$

However, since $\bar{J}_1$ is of form

$$\bar{J}_1 = \bar{j}_1 \chi'_1 + \bar{j}_1 \chi'_2.$$

chain rule has to be applied in order to express everything consistently in molar concentrations, which yields

$$\bar{J}_1 = \left[\bar{j}_1 \frac{\partial \chi_1}{\partial c_1} + \bar{j}_2 \frac{\partial \chi_2}{\partial c_1} \right] c'_1 + \left[\bar{j}_1 \frac{\partial \chi_1}{\partial c_2} + \bar{j}_2 \frac{\partial \chi_2}{\partial c_2} \right] c'_2 = \bar{j}_{11} c'_1 + \bar{j}_{12} c'_2. \quad (\text{B7})$$

after reordering of terms. Using (B7) in (B6) gives the final version of the weak form, which reads in short hand notation

$$\langle (c_1, c_2), (v, w) \rangle - \langle (\bar{j}_{11} c'_1 + \bar{j}_{12} c'_2, 0), (v', w') \rangle \Delta t + \langle (\bar{r}_1, \bar{r}_2), (v, w) \rangle \Delta t = \langle ({}^m c_1, {}^m c_2), (v, w) \rangle \quad (\text{B8})$$

with the operator $\langle (a_1, b_1), (a_2, b_2) \rangle$ defined by

$$\langle (a_1, b_1), (a_2, b_2) \rangle := \int_0^h [a_1 b_1 + a_2 b_2] \, dz.$$