C – Mathematical reformulation

The following system of partial differential equations with initial and boundary conditions describes problem of interdiffusion (for the details - see section B)

$$\begin{aligned}
&\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x},\\
&J_i = -\sum_{k=1}^{r} D_{i,k}(c_1,\ldots,c_r)\frac{\partial c_k}{\partial x} + c_i K(t) + c_i \upsilon,\\
&D_{i,k}(c_1,\ldots,c_r) := D_i^*(c_1,\ldots,c_r)c_i \frac{\partial \ln a_i(c_1,\ldots,c_r)}{\partial c_k},\\
&J_i(0,t) = J_i(d,t) = 0,\\
&c_i(x,0) = c_i^0(x),\\
&for\ \ i = 1,\ldots,r,\ \ t \ge 0,\ \ x \in [0,\ d]
\end{aligned} \tag{1}$$

$$where\ \ \upsilon = \frac{1}{c}\sum_{k,l=1}^{r} D_{k,l}(c_1,\ldots,c_r)\frac{\partial c_l}{\partial x} \tag{2}$$

In this section mathematical reformulation of the problem given by eqns. (1)-(2) suitable for obtaining solution to the problem is presented.

Let us introduce the following notation:

$$\begin{aligned}
&\overline{x} = x / x_s,\ \overline{t} = t / t_s,\ \ \overline{c}_i(\overline{x},\overline{t}) = c_i(x_s\overline{x}, t_s\overline{t}) / c_s,\ \ \overline{J}_i(\overline{x},\overline{t}) = J_i(x_s\overline{x}, t_s\overline{t}) / J_s.\\
&where\ \ x_s, t_s, c_s, J_s\ \ -\ \ characteristic\ values
\end{aligned} \tag{3}$$

Using (3) we can calculate:

$$\begin{aligned}
&\frac{\partial \overline{c}_i}{\partial \overline{t}}(\overline{x},\overline{t}) = \frac{\partial c_i}{\partial t}(x_s\overline{x}, t_s\overline{t})\frac{t_s}{c_s},\\
&\frac{\partial \overline{c}_i}{\partial \overline{x}}(\overline{x},\overline{t}) = \frac{\partial c_i}{\partial x}(x_s\overline{x}, t_s\overline{t})\frac{x_s}{c_s},\\
&\frac{\partial \overline{J}_i}{\partial \overline{x}}(\overline{x},\overline{t}) = \frac{\partial J_i}{\partial x}(x_s\overline{x}, t_s\overline{t})\frac{x_s}{J_s},
\end{aligned} \tag{4}$$

Using (4) we can rewrite equations (1)

$$\frac{\partial \overline{c}_i}{\partial \overline{t}} = -\frac{J_s t_s}{c_s x_s}\frac{\partial \overline{J}_i}{\partial \overline{x}}.$$

Rescaling of fluxes

$$\overline{J}_i = -\frac{c_s}{J_s x_s}\sum_{k=1}^{r} D_{i,k}(c_s\overline{c}_1,\dots,c_s\overline{c}_r)\frac{\partial \overline{c}_k}{\partial x} + \frac{c_s}{J_s}\overline{c}_i K(t_s\overline{t}) + \frac{t_s c_s^2}{J_s x_s}\frac{\overline{c}_i}{c}\sum_{k,l=1}^{r} D_{k,l}(c_s\overline{c}_1,\dots,c_s\overline{c}_r)\frac{\partial \overline{c}_l}{\partial \overline{x}}.$$

If we substitute $J_s = \frac{c_s x_s}{t_s}$, then we get

$$\overline{J}_i = -\frac{t_s}{x_s^2}\sum_{k=1}^{r} D_{i,k}(c_s\overline{c}_1,\dots,c_s\overline{c}_r)\frac{\partial \overline{c}_k}{\partial x} + \frac{t_s}{x_s}\overline{c}_i K(t_s\overline{t}) + \frac{t_s c_s}{x_s^2}\frac{\overline{c}_i}{c}\sum_{k,l=1}^{r} D_{k,l}(c_s\overline{c}_1,\dots,c_s\overline{c}_r)\frac{\partial \overline{c}_l}{\partial \overline{x}}.$$

On introducing functions

$$\overline{D}_{i,k}(\xi_1,\dots,\xi_r) = \frac{t_s}{x_s^2} D_{i,k}(c_s\xi_1,\dots,c_s\xi_r),$$

$$\overline{K}(\overline{t}) = \frac{t_s}{x_s} K(t_s\overline{t}),$$

we obtain the following rescaled (non-dimensionless) system:

Equations

$$\frac{\partial \overline{c}_i}{\partial \overline{t}} = -\frac{\partial \overline{J}_i}{\partial \overline{x}},$$

where

$$\overline{J}_i = -\sum_{k=1}^{r} \overline{D}_{i,k}(\overline{c}_1,\dots,\overline{c}_r)\frac{\partial \overline{c}_k}{\partial \overline{x}} + \overline{c}_i\overline{K}(\overline{t}) + \frac{c_s}{c}\overline{c}_i\sum_{k,l=1}^{r} \overline{D}_{k,l}(\overline{c}_1,\dots,\overline{c}_r)\frac{\partial \overline{c}_l}{\partial \overline{x}}.$$

Boundary conditions

$$\begin{cases} \overline{J}_i(0,\overline{t}) = \overline{j}_i^0(\overline{t}), \\ \overline{J}_i(d,\overline{t}) = \overline{j}_i^d(\overline{t}) \end{cases}$$

where $\overline{j}_i^0(\overline{t}) = \frac{t_s}{x_s} j_i^0(t_s\overline{t}),\ \overline{j}_i^d(\overline{t}) = \frac{t_s}{x_s} j_i^d(t_s\overline{t}).$

Initial conditions

$$\overline{c}_i(\overline{x},0)=\overline{c}_i^{\,0}(\overline{x}),$$

where $\overline{c}_i^{\,0}(\overline{x})=c(x_s\overline{x})/c_s$ for $\overline{x}\in[0,\ \overline{d}\,]$.

If activities are given as functions of species mole fractions

$$a_i(c_1,\ldots,c_r)=\tilde{a}(N_1(c_1,\ldots,c_r),\ldots,N_{r-1}(c_1,\ldots,c_r)),$$
$$\frac{\partial\ln a_i}{\partial c_k}=\sum_{j=1}^{r-1}\frac{\partial\ln\tilde{a}_i}{\partial N_j}\frac{\partial N_j}{\partial c_k}.$$

But $N_j=\dfrac{c_k}{c_1+\ldots+c_r}$, so

$$\frac{\partial N_j}{\partial c_k}=\frac{\delta_{k,j}\sum_{l=1}^{r}c_l-c_j}{\left(\sum_{l=1}^{r}c_l\right)^2}=\frac{\delta_{k,j}c-c_j}{c^2},$$

or

$$\frac{\partial N_j}{\partial c_k}=\begin{cases}\dfrac{1}{c}-\dfrac{c_j}{c^2} & dla\ \ k=j,\\[2mm] \dfrac{c_j}{c^2} & dla\ \ k\neq j.\end{cases}$$