

Documentation of ParScale's Chemistry Models

Note, that the following documentation is mainly based on the nomenclature used by: Melchiori, Canu: *Improving the Quantitative Description of Reacting Porous Solids: Critical Analysis of the Shrinking Core Model by Comparison to the Generalized Grain Model*, Industrial and Engineering Chemistry Research, 2013.

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1 Nomenclature

1.1 Latin Characters

Table 1: Used variables

| Variable | Unit | Meaning |
|----------------------|------------------------------------|---|
| a, b, c, d | | Stoichiometric coefficients of generic reaction |
| A, B, C, D | | Species of generic reaction |
| a_0 | m^{-1} | Initial surface-volume ratio of the solid reagent in the particle |
| \mathbb{B} | s m^{-2} | Inverse StefanMaxwell diffusion matrix |
| c | kmol m^{-3} | Concentration |
| D | $\text{m}^2 \text{s}^{-1}$ | Molecular (binary) diffusion coefficient |
| \underline{D}_{ij} | $\text{m}^2 \text{s}^{-1}$ | Effective binary diffusion coefficient of i in j |
| $f(X)$ | | Local abundance of solid per unit volume of porous solid |
| J^* | $\text{kmol m}^{-2} \text{s}^{-1}$ | Diffusive molar flux |
| k | s^{-1} | Volumetric kinetic constant of CM |
| MW | kg kmol^{-1} | Molecular weight of i |
| \dot{n} | $\text{kmol m}^{-2} \text{s}^{-1}$ | Molar flux |
| $NG/NL/NS/NR$ | | Total number of gas/liquid/solid species and reactions |
| r | m | Radial particle coordinate |
| R | $\text{J kmol}^{-1} \text{K}^{-1}$ | Universal gas constant (8314.41) |
| s | $\text{kmol m}^{-3} \text{s}^{-1}$ | Chemical production rate per unit total volume |
| T | K | Temperature |
| t | sec | Time |
| x | | Molar fraction |
| X | | Solid conversion |

1.2 Greek Characters

| Variable | Unit | Meaning |
|----------------|--------------------|---|
| α_s | | Sintering factor |
| γ_i | | Mass fraction of species i in the porous solids |
| $\delta_{i,j}$ | | Kronecker delta function (=1 if $i = j$ and zero otherwise) |
| ε | | Phase fraction (volume-based) |
| $\nu_{i,j}$ | | Stoichiometric coefficient of species |
| τ | | Tortuosity |
| ρ | kg m^{-3} | Density |

1.3 Superscripts

| Variable | Meaning |
|----------|----------------|
| n | Reaction order |

1.4 Subscripts

| Variable | Meaning |
|----------|------------------|
| A | Apparent |
| $g/l/s$ | Gas/Liquid/Solid |
| $grain$ | Grain |
| i | Species index |
| I | Intrinsic |
| j | Reaction index |
| K | Knudsen |
| $pore$ | Pore |
| tot | Total |

2 Continuous Model (CM)

The present analysis is made by the assumption of a generic reaction in which a solid species A and a gas species B yields a solid and gas species through the irreversible reaction:



Examples can be found e.g. at the reduction of iron oxides by H_2 , calculations of ZnS and FeS with O_2 to metal oxides (ZnO , Fe_2O_3) and combustion of coal in order to give Co and ash. The mass balance equation for a single gaseous species in a porous particle is written as (negilate source due to possible phase change):

$$\frac{\partial}{\partial t}(\varepsilon_g c_g) + \nabla \cdot \dot{n}_g = \sum_{i=1}^{NG} (s_{g,i}). \quad (2.2)$$

which could be solved together with the total mass equation

$$\frac{\partial}{\partial t} c = -\nabla \cdot \dot{n} + \sum_{i=1}^{NR} s_i \quad (2.3)$$

A typical model for s_i is

$$s_i = \sum_{j=1}^{NR} \nu_{ij} \cdot \prod_i^{NG+NS} c_k^{n_{i,j}} \quad (2.4)$$

Note that in parScale no total mass equation is solved at the moment. The mass balance equations for the solid phase are as follows (negilate source due to possible phase change):

$$\frac{\partial}{\partial t} c_{s,i} = s_{s,i} \quad (2.5)$$

The molar flow of a single gas species can be expressed as the sum of diffusive and convective terms:

$$\dot{n}_i = x_i \dot{n} + J_i^* \quad (2.6)$$

As the gaseous reaction are mostly highly concentrated in the gas phase (no dilutes) the diffusive flux requires the generalized Flick law:

$$J_i^* = -c_{g,tot} \sum_{i=1}^{NG-1} \mathbb{D}_{ij} \frac{\partial x_i}{\partial r} \quad (2.7)$$

For details of the implementation regarding the convective flux see `/doc/pdf/1modelEqn/00basemodeleqn.pdf`. The matrix \mathbb{D}_{ij} must be calculated according to the multi-component Stephan-Maxwell theory depending on the binary diffusion coefficients, the local composition and therefore as a inverse of \mathbb{B} :

$$\mathbb{D} = \mathbb{B}^{-1} \quad (2.8)$$

with

$$\mathbb{B}_{ij} = \frac{x_i}{\underline{D}_{iNG}} + \delta_{ij} \left(\frac{1}{D_i^K} + \sum_{k=1, k \neq i}^{NG} \frac{x_k}{\underline{D}_{ik}} \right) + (\delta_{ij} - 1) \frac{x_i}{\underline{D}_{ij}} \quad (2.9)$$

where Knudsen and molecular diffusion ($\underline{D}_{ik}, \underline{D}_{ij}$) are included. \underline{D}_{ij} can be calculated as a function of a local porosity and tortuosity of the solid as follows:

$$\underline{D}_{ij} = D_{ij} \frac{\varepsilon}{\tau} \quad (2.10)$$

Note that no refinement model for diffusion is currently implemented in **parScale**. \mathbb{D}_{ij} is only depending only depending on the local phase fractions and tortuosities (compare Eqn. (2.10)). If wanted, Knudsen diffusion can be activated in order to better account for diffusion processes in porous particles (see `/doc`). The Knudsen diffusion coefficient is calculated using the following equation:

$$D_{K,i,pore} = r_{i,pore} \frac{2}{3} \sqrt{\frac{8}{\pi} \frac{RT}{MW_i}} \quad (2.11)$$

taken into account for the effective diffusion coefficient:

$$\underline{D}_{K,i,pore} = D_{K,i,pore} \frac{\varepsilon}{\tau} \quad (2.12)$$

$$\mathbb{D}_{ij} = \frac{1}{\frac{1}{\underline{D}_{K,i,pore}} + \frac{1}{\underline{D}_{ij}}} \quad (2.13)$$

Normally tortuosity is considered as a parameter and porosity is depending on the degree of conversion of the solid. This can be due to eventually different densities. Under the assumption of a particle with constant volume, the porosity can be calculated using the intrinsic and apparent densities of the solid

$$\varepsilon = 1 - \frac{\rho_A}{\rho_I} \quad (2.14)$$

where the densities can be calculated as follows:

$$\rho_A = \sum_{j=1}^{NS} c_j MW_j \quad (2.15)$$

The equation of the total concentration (eqn. (2.3)) is solved in the total molar flux \dot{n} under the knowledge of an analytic calculation depending on the solid source term:

$$\rho_I = \left(\sum_{j=1}^{NS} \frac{\gamma_j}{\rho_{I,j}} \right)^{-1} = \left(\sum_{j=1}^{NS} \left(\frac{1}{\rho_{I,j}} \frac{c_j MW_j}{\sum_{i=1}^{NS} c_i MW_i} \right) \right)^{-1} \quad (2.16)$$

After a combination of eqn (2.15) and ((2.16)) the local, composition dependent porosity drops out as:

$$\varepsilon = 1 - \sum_{j=1}^{NS} c_j \frac{MW_j}{\rho_{I,j}} \quad (2.17)$$

$$\frac{\partial \varepsilon c}{\partial t} = -c \sum_{j=1}^{NS} s_j \frac{MW_j}{\rho_{I,j}} \quad (2.18)$$

Mass is conservative, so the mass gain of the gas phase is due to the mass loss in the solid phase. The equation is only valid in cases of constant ambient conditions such as pressure and temperature. If these conditions change the total gas concentration can be calculated using the ideal gas law:

$$c = \frac{p}{RT} \quad (2.19)$$

The production rate of every species can be calculated as:

$$s_i = a R \quad (2.20)$$

Also it includes a nonlinear function of solid conversion X :

$$R = k f(X) c_B \quad (2.21)$$

$$X = 1 - \frac{c_A}{c_{A,0}} \quad (2.22)$$

In this equation k is the kinetic constant and $f(X)$ describes the local abundance of solid A per unit volume of porous solid. Due to the heterogeneous nature of the underlying reaction the surplus amount of A highly depends on the local structure of the porous solid. This function can be expressed by making some assumptions on the evolution of the solid matrix due to the reaction. For this micro spherical grains a shrinking core model is used for the solid reactant as proposed and used in several publications. It considers the local geometry and microscopic structure inside the particle and can be described as:

$$f(X) = \left[(1 - X)^{-2/3} + b \frac{k r_{grain}}{a_0 D_{B,grain}} (1 - X)^{-1/3} + b \frac{k r_{grain}}{a_0 D_{B,grain}} \right]^{-1} \quad (2.23)$$

This equation includes both kinetic and intragrain diffusion resistances where $D_{B,grain}$ is the effective diffusivity of the gaseous reactant into the grain product layer, r_{grain} is the grain radius and a_0 is the ratio between the initial surface of the solid reactant into the particle and the total volume of the particle itself. If only the kinetic component is taken into account, eqn (2.23) simplifies as follows:

$$f(X) = (1 - X)^{2/3} \quad (2.24)$$

This is valid only if there is no important diffusion inside resistance inside the micro grains. Furthermore the kinetic expression does not depend on the grain size itself which makes it applicable to non spherical grains (e.g. $\alpha = 0.5$ for cylindrical, $\alpha = 0$ for planar slabs) in the equation:

$$f(X) = (1 - X)^\alpha \quad (2.25)$$

For the grain model $f(X)$ it is the ratio between the spherical surface of the unreacted core of the micro grain and the total external surface of the grain.