

Documentation on Chemistry Models

Note that the following documentation is mainly based on: 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		Stoichiometric coefficient of the solid reagent
a_0	m^{-1}	Initial surface-volume ratio of the solid reagent in the particle
b		Stoichiometric coefficient of the gaseous reagent
\mathbb{B}	s m^{-2}	Inverse StefanMaxwell diffusion matrix
c_A	kmol m^{-3}	Solid molar concentration of species A
c, c_B, c_B^*	$\text{kmol m}^{-3}_{\text{total}}$	Gas molar concentration, total, of species B, at the coreshell interface
\mathbb{D}	$\text{m}^2 \text{s}^{-1}$	Stefan- Maxwell diffusion matrix
\underline{D}_{ij}	$\text{m}^2 \text{s}^{-1}$	Effective binary diffusion coefficient of i in j
D_{ij}	$\text{m}^2 \text{s}^{-1}$	Molecular binary diffusion coefficient of i in j
D_i^K	$\text{m}^2 \text{s}^{-1}$	Knudsen diffusion coefficient of i
$D_{B,g}$	$\text{m}^2 \text{s}^{-1}$	Effective diffusion coefficient of B in the grain
J_i^*	$\text{kmol m}^{-2} \text{s}^{-1}$	Diffusive molar flux of i
k	l s^{-1}	Volumetric kinetic constant of CM
MW_i	kg kmol^{-1}	Molecular weight of i (g/mol)
N, N_i	$\text{kmol m}^{-2} \text{s}^{-1}$	(Convective plus diffusive) molar flux of gas, total and of species i
NG		Total number of gas species
NS		Total number of solid species
r, r^*, r_0	m	Radial particle coordinate; generic, at the reaction interface for SCM, initial
r_g	m	Grain radius
R	$\text{kmol m}^{-3} \text{s}^{-1}$	Reaction rate per unit volume of porous solid
s_i	$\text{kmol m}^{-3} \text{s}^{-1}$	Production rate of the species i per unit volume of porous solid
T	K	Temperature
x_i		Molar fraction of species i in the porous solids
X		Solid conversion
γ_i		Mass fraction of species i in the porous solids

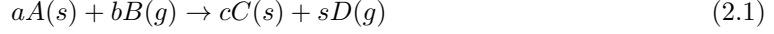
1.2 Greek Characters

Table 2: Used variables

Variable	Unit	Meaning
α		Sintering factor
δ		Kroneckers delta (=1 if $i = j$ and zero otherwise)
ε		Porosity
ν_j		Stoichiometric coefficient of j (can be solid or gas)
τ		Tortuosity
ρ_A, ρ_I	kg m^{-3}	Apparent and intrinsic mass density of the solid

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 species in a porous particle is written as:

$$\frac{\partial \varepsilon c_i}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_i) + s_i \text{ with } i = B, D \quad (2.2)$$

which could be solved together with the total mass equation

$$\frac{\partial \varepsilon c}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N) + \sum_{j=1}^{NG} S_j \quad (2.3)$$

Note that in parScale no total mass equation is solved at the moment. The mass balance equations for the solid phase are as follows:

$$\frac{\partial \varepsilon c_i}{\partial t} = s_i \text{ with } i = A, C \quad (2.4)$$

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

$$N_i = x_i N + J_i^* \quad (2.5)$$

Note that in the current implementation no convective flux inside the particle is considered which simplifies eqn (2.5) to

$$N_i = J_i^* \quad (2.6)$$

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

$$J_i^* = -c \sum_{j=1}^{NG-1} \mathbb{D}_{ij} \frac{\partial x_j}{\partial r} \quad (2.7)$$

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

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

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 and all properties are assumed to be constant. 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

$$\varepsilon = 1 - \frac{\rho_A}{\rho_I} \quad (2.11)$$

where the densities can be calculated as follows:

$$\rho_A = \sum_{j=1}^{NS} c_j MW_j \quad (2.12)$$

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

$$\rho_I = \left(\sum_{j=1}^{NS} \frac{\gamma_j}{\rho_{I,j}} \right)^{-1} = \left(\sum_{j=1}^{NS} \left(\frac{1}{\rho_{I,j}} \frac{c_j MW_j}{\sum_{i=1}^{NS} c_i MW_i} \right) \right)^{-1} \quad (2.13)$$

After a combination of eqn (2.12) and ((2.13)) the local, composition dependent porosity drops out as:

$$\varepsilon = 1 - \sum_{j=1}^{NS} c_j \frac{MW_j}{\rho_{I,j}} \quad (2.14)$$

$$\frac{\partial \varepsilon c}{\partial t} = -c \sum_{j=1}^{NS} s_j \frac{MW_j}{\rho_{I,j}} \quad (2.15)$$

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:

$$c = \frac{P}{R_g T} \quad (2.16)$$

The production rate of every species can be calculated as:

$$s_i = \nu_j R \quad (2.17)$$

That equation is valid under the assumption of a first order reaction whereby R is described assuming irreversibility and first order in the concentration of the gas reactant. Also it includes a nonlinear function of solid conversion X :

$$R = k f(X) c_B \quad (2.18)$$

$$X = 1 - \frac{c_A}{c_A^0} \quad (2.19)$$

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 amount of superficial 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:

$$f(X) = \left[(1 - X)^{-2/3} + b \frac{k r_g}{a_0 D_{B,g}} (1 - X)^{-1/3} + b \frac{k r_g}{a_0 D_{B,g}} \right]^{-1} \quad (2.20)$$

This equation includes both kinetic and intragrain diffusion resistances where $D_{B,g}$ is the effective diffusivity of the gaseous reactant into the grain product layer, r_g 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 (2.20) simplifies as follows:

$$f(X) = (1 - X)^{2/3} \quad (2.21)$$

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:

$$f(X) = (1 - X)^\alpha \quad (2.22)$$

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.