

3 Modelling of Stirred Reactors

In this chapter the fundamental aspects related to the modelling of stirred reactors are presented. These aspects cover basic definitions about the gas system, the principles of gas phase thermochemistry, the balance equations from continuum mechanics, two models for a spatially homogeneous transient reactor and a geometrical interpretation of the chemical reactors equations on the basis of the theory of dynamical systems. The presentation of the chemical transformation assumes that the continuum hypothesis is valid for the reactive gas mixture when such a mixture flows through a control volume.

3.1 Fundamental Definitions

The *molar fraction* of the i -th chemical species is defined as

$$X_i \equiv \frac{n_i}{n}, \quad (3.1)$$

where n_i is the number of moles of the i -th chemical species, n is the system total number of moles, i.e.,

$$n \equiv \sum_{i=1}^{n_s} n_i, \quad (3.2)$$

where n_s is the number of chemical species. It follows from the definition that X_i satisfies

$$0 \leq X_i \leq 1, \quad \text{and} \quad \sum_{i=1}^{n_s} X_i = 1. \quad (3.3)$$

The *mass fraction* of the i -th chemical species is defined as

$$Y_i \equiv \frac{m_i}{m}, \quad (3.4)$$

where m_i is the i -th chemical species mass and m is the system total mass, i.e.,

$$m \equiv \sum_{i=1}^{n_s} m_i. \quad (3.5)$$

It follows straightforward from the definition, that Y_i satisfies

$$0 \leq Y_i \leq 1, \quad \text{and} \quad \sum_{i=1}^{n_s} Y_i = 1. \quad (3.6)$$

The *molar mass* of the i -th chemical species, W_i , is defined as the mass of 1 mol of this species, i.e., N_A particles, where $N_A = 6.023 \times 10^{23}$ is the *Avogadro number*. The sum of the molar masses of all the species that compose a homogeneous gas mixture weighted by the molar fraction is the *mean molar mass* of the mixture,

$$\bar{W} \equiv \sum_{i=1}^{n_s} X_i W_i. \quad (3.7)$$

Mass fraction and molar fraction are two different concepts used to describe the amount of a chemical species in a gas mixture, and may be related with the help of \bar{W} and W_i ,

$$Y_i = \frac{W_i}{\bar{W}} X_i. \quad (3.8)$$

The *molar concentration* of the chemical species i is defined as

$$C_i \equiv \frac{n_i}{V}, \quad (3.9)$$

where V is the volume of the system, whereas the *mixture concentration* is defined as

$$C \equiv \sum_{i=1}^{n_s} C_i = \frac{n}{V}. \quad (3.10)$$

The *partial density* of the chemical species i is defined as

$$\rho_i \equiv \frac{m_i}{V}, \quad (3.11)$$

whereas the *mixture density*, or *density*, is defined as

$$\rho \equiv \sum_{i=1}^{n_s} \rho_i = \frac{m}{V}. \quad (3.12)$$

Density and concentration are intensive properties of a gas mixture, which are related via

$$\rho = \bar{W} C. \quad (3.13)$$

3.2 Gas Phase Thermochemistry

3.2.1 Equation of State for Perfect Gases

A perfect gas is a model to describe a gas that is composed by a set of point particles moving randomly that interact only through elastic collisions. This class of gases obeys an equation of state relating temperature, pressure and density called ideal gas law, which is given by

$$pV = nRT, \quad (3.14)$$

where p is the *pressure*, R is the *universal gas constant* and T is the *temperature*.

A consequence of the perfect gas model is that all the intensive thermodynamical properties are known function of the mixture temperature only. Herein it will be assumed that all the gas mixtures are composed by gases that behave as a perfect gas.

3.2.2 Stoichiometry

A gas mixture is said to be *stoichiometric* if the fuel and the oxidizer are in a proportion that are completely consumed during the reaction. If there is an excess of fuel, the mixture is called *fuel-rich*, and if there is an excess of oxidizer, it is called *fuel-lean* (Warnatz et al., 1999) [95].

The *equivalence ratio* is defined as

$$\Phi \equiv \frac{\frac{X_{Fu}}{X_{Ox}}}{\left(\frac{X_{Fu}}{X_{Ox}}\right)_{st}}, \quad (3.15)$$

where X_{Fu} is the fuel molar fraction, X_{Ox} is the oxidizer molar fraction and the subscript $_{st}$ notes stoichiometric conditions. By definition, Φ is smaller than one if the mixture is fuel-lean, greater than one if the mixture is fuel-rich and unitary if the mixture is stoichiometric, i.e.,

$$\begin{aligned} \Phi < 1 & \quad \text{fuel - lean mixture,} \\ \Phi = 1 & \quad \text{stoichiometric mixture,} \\ \Phi > 1 & \quad \text{fuel - rich mixture.} \end{aligned} \quad (3.16)$$

3.2.3 Reaction Mechanism

During a chemical transformation the molecular bonds holding atoms in a given molecule are broken and new bonds are formed with other molecules, leading to a conversion process between bond and kinetic energy. The number of atoms does not change in this transformation (Zel'dovich et al., 1985) [99].

A reaction mechanism with n_r elementary reactions and n_s chemical species can be represented in the general form

$$\sum_{i=1}^{n_s} \nu'_{ij} \mathcal{M}_i \rightleftharpoons \sum_{i=1}^{n_s} \nu''_{ij} \mathcal{M}_i, \quad j = 1, \dots, n_r, \quad (3.17)$$

where \mathcal{M}_i is the symbol of the i -th chemical species and the integers ν'_{ij} and ν''_{ij} are, respectively, the forward and reverse stoichiometric coefficients of chemical species i in the j -th elementary reaction. The Table 3.1 presents a chemical kinetics mechanism, with 4 species (CO , O , CO_2 and O_2) and 3 reactions, for the description of carbon monoxide oxidation (Gardiner, 2000) [21].

Table 3.1: Reaction mechanism for carbon monoxide (CO) oxidation. In this table M represent a third body with a specific efficiency for each species ($f_{O_2} = 0.4$, $f_{CO} = 0.75$ and $f_{CO_2} = 1.5$).

Reaction	A_i (cm, mol, s)	β_i	E_i (cal/mol)
1: $O_2 + CO \rightleftharpoons CO_2 + O$	1.260×10^{13}	0.00	23682.94
2: $CO + O + M \rightleftharpoons CO_2 + M$	1.540×10^{15}	0.00	1510.70
3: $O + O + M \rightleftharpoons O_2 + M$	5.400×10^{13}	0.00	-899.69

Further information about reaction mechanisms can be obtained in the work of Orbegoso et al. (2009) [65], that presents a survey of recent chemical kinetics mechanisms available to model the combustion of simple fuels, such as hydrogen, natural gas, Syngas and liquefied petroleum gas.

3.2.4 Rate of Reaction

The transition from the initial to the final state is characterized by the chemical reaction rates for the various species of the reaction mechanism. The *net production rate* $\dot{\omega}_i$ of the i -th chemical species in a multistep mechanism is given by

$$\dot{\omega}_i = \sum_{j=1}^{n_r} \nu_{ij} r_j, \quad (3.18)$$

where the *overall stoichiometric coefficients* are

$$\nu_{ij} = \nu_{ij}'' - \nu_{ij}', \quad (3.19)$$

and the *overall reaction rate* of the j -th elementary reaction, r_j , is given by

$$r_j = r_j^+ - r_j^-, \quad (3.20)$$

where the *forward reaction rate* r_j^+ and the *reverse reaction rate* r_j^- are given by

$$r_j^+ = k_j^+ \prod_{i=1}^{n_s} C_i^{\nu_{ij}'}, \quad \text{and} \quad r_j^- = k_j^- \prod_{i=1}^{n_s} C_i^{\nu_{ij}''}, \quad (3.21)$$

with k_j^+ and k_j^- being the rate constants for the forward and reverse j -th elementary reaction.

The forward rate constant for the j -th elementary reaction is assumed to evolve according to an *Arrhenius law* (Williams, 1985) [96],

$$k_j^+ = A_j T^{\beta_j} \exp\left(-\frac{E_j}{RT}\right), \quad (3.22)$$

where A_j is the *pre-exponential factor*, of the j -th elementary reaction, which is representative of the molecular collision frequency at the average thermal velocity, β_j is *temperature exponent* of the j -th reaction and E_j is the *activation energy* of the j -th elementary reaction, which describes a barrier of energy that has to be overcome during the reaction.

The reverse rate constant for the j -th elementary reaction is related to the forward rate and its determination will be given in the following subsection.

3.2.5 Thermochemical Equilibrium

When the forward and the reverse reaction rate of the j -th elementary reaction approach each other, the concentration of the chemical species ceases to change and the system reaches a state of dynamic equilibrium (Zel'dovich et al., 1985) [99], which can be expressed as

$$0 = k_j^+ \prod_{i=1}^{n_s} C_i^{\nu_{ij}^+} - k_j^- \prod_{i=1}^{n_s} C_i^{\nu_{ij}^-}, \quad (3.23)$$

which yields

$$K_{c_j} \equiv \frac{k_j^+}{k_j^-} = \frac{\prod_{i=1}^{n_s} C_i^{\nu_{ij}^-}}{\prod_{i=1}^{n_s} C_i^{\nu_{ij}^+}} = \prod_{i=1}^{n_s} C_i^{\nu_{ij}}, \quad (3.24)$$

which defines the j -th elementary reaction *equilibrium constant in concentration units*, K_{c_j} . Note that it is also possible to define the j -th elementary reaction equilibrium constants in terms of pressure units,

$$K_{p_j} \equiv \prod_{i=1}^{n_s} p_i^{\nu_{ij}}, \quad (3.25)$$

and it is easy to show that the two equilibrium constants are related by

$$K_{c_j} = K_{p_j} \left(\frac{p^o}{RT} \right)^{\sum_{i=1}^{n_s} \nu_{ij}}, \quad (3.26)$$

where p^o is the *pressure at the standard state*.

From the definition of the *Gibbs free energy* (Warnatz et al., 1999) [95], it is possible to show that

$$K_{p_j} = \exp \left(\frac{\Delta S_j^o}{R} - \frac{\Delta H_j^o}{RT} \right), \quad (3.27)$$

where the *net change in entropy* ΔS_j^o and the *net change in enthalpy* ΔH_j^o in the j -th reaction are respectively given by

$$\Delta S_j^o \equiv \sum_{i=1}^{n_s} \nu_{ij} S_i^o, \quad (3.28)$$

and

$$\Delta H_j^o \equiv \sum_{i=1}^{n_s} \nu_{ij} H_i^o. \quad (3.29)$$

For all chemical species, the *enthalpy of formation* H_i^o and *entropy in standard state* S_i^o are assumed to be known functions of temperature and can be calculated, for example, using Chemkin-II package (Kee et al., 1989) [37].

3.3 Equations of Balance

Classically, the fundamental principles of balances (mass, momentum, chemical species and energy) are mathematically formulated in terms of partial differential equations. These fundamental principles are presented here without development, which may be found elsewhere Williams (1985) [96] or Law (2006) [45].

The balance equations of the total mass, momentum, species mass and energy read

$$\frac{\partial \rho}{\partial t} = \Gamma_\rho, \quad (3.30)$$

$$\frac{\partial(\rho \mathbf{u})}{\partial t} = \Gamma_{\mathbf{u}}, \quad (3.31)$$

$$\frac{\partial(\rho Y_i)}{\partial t} = \Gamma_{Y_i} + \Omega_i, \quad i = 1, \dots, n_s, \quad (3.32)$$

$$\frac{\partial(\rho h)}{\partial t} = \Gamma_h, \quad (3.33)$$

where t is the time; Γ_ρ represents the mass convection; \mathbf{u} is the velocity field; $\Gamma_{\mathbf{u}}$ accounts for the momentum convection, external surface and body forces; Γ_{Y_i} describes the convective and diffusive transport of the i -th chemical species; Ω_i is the i -th chemical species source term; h is the specific enthalpy and Γ_h accounts for all mechanisms of energy transport, i.e., conduction, convection and radiation. These equations are supplemented by the equation of state, Eq.(3.14), appropriate boundary and initial conditions.

3.4 Partially Stirred Reactor with IEM Model

A *partially stirred reactor* (PaSR) is a spatially homogeneous, transient, reactor model governed by the competition of chemical reactions, turbulent mixing and the *residence time* within the reactor, defined as

$$\tau_r \equiv \frac{\rho V}{\dot{m}}, \quad (3.34)$$

where \dot{m} is the *mass flow rate* entering the reactor. In such a reactor, a statistically steady state of “unmixedness” may be maintained. In this sense, this reactor is a chemical equivalent of the nondecaying homogeneous turbulent flow, in which energy is continuously supplied to the system in order to maintain the turbulence (Correa, 1993) [13].

A particular solution to such a reactor considers Monte-Carlo techniques, in which the reactive system consists of n_p stochastic particles, evolving adiabatically and at constant pressure. Under such hypothesis, $\Gamma_\rho = \Gamma_{\mathbf{u}} = 0$,

and the equation of state determines the density for a given temperature and mixture composition. The terms of enthalpy transport Γ_h and of the chemical species Γ_{Y_i} describe the turbulent transport micromixing process (Pope, 1985) [69]. Thus, under the hypothesis of linear relaxation of the properties towards the mean value, the balance equations for the the j -th stochastic particle ($j = 1, \dots, n_p$) of this system read

$$\frac{dh^{(j)}}{dt} = -\frac{h^{(j)} - \langle h \rangle}{\tau_m}, \quad (3.35)$$

$$\frac{dp^{(j)}}{dt} = 0, \quad (3.36)$$

$$\frac{dY_i^{(j)}}{dt} = -\frac{Y_i^{(j)} - \langle Y_i \rangle}{\tau_m} + \frac{\dot{\omega}_i^{(j)} W_i}{\rho}, \quad i = 1, \dots, n_s, \quad (3.37)$$

where the superscript (j) denote the j -th stochastic particle, τ_m is the *mixing time*, $\langle h \rangle$ and $\langle Y_i \rangle$ denote the *ensemble average* of h and Y_i respectively, where the ensemble average operator is defined as

$$\langle \psi \rangle \equiv \frac{1}{n_p} \sum_{j=1}^{n_p} \psi^{(j)}, \quad (3.38)$$

being ψ a generic property of the reactive system.

Another statistical quantity that is useful in the description of a system with stochastic particles is the *ensemble variance*, whereas the ensemble variance operator is defined as

$$\langle \psi'^2 \rangle \equiv \frac{1}{n_p} \sum_{j=1}^{n_p} (\psi^{(j)} - \langle \psi \rangle)^2, \quad (3.39)$$

and can be shown that

$$\langle \psi'^2 \rangle = \langle \psi^2 \rangle - \langle \psi \rangle^2. \quad (3.40)$$

Note that the micromixing process has been described in Eq.(3.37) by the interaction by exchange with the mean (IEM) model. More details about mixing models can be found in Fox (2003) [18]. The second term on the right hand side of Eq.(3.37) is the reaction rate of the i -th chemical species. The modelling of this nonlinear term has been described in section 3.2.4 and introduces stiffness on the chemical system, since the associated range of time scales spans over several orders of magnitude (Correa, 1993) [13].

3.5

Pairwise Mixing Stirred Reactor

According to Pope (1997) [70], for the purpose of testing a chemical kinetic reduction technique, it is desirable to devise a mixing model that leads to a

composition region accessed during the solution process which is “wider” than that provided by the IEM model.

Therefore, Pope (1997) [70] proposed the *pairwise mixing stirred reactor* (PMSR), which is designed to yield a much larger accessed region, and hence should provide a stringent test to the ability of the reduction technique to yield a reduction in computational time.

In the PMSR model the reactor consists of an even number n_p of particles. Given a time step, Δt , the model describes three types of events, for each discrete times $k\Delta t$, where k is an integer, *inflow*, *outflow* and *pairing*.

Initially, the particles are arranged in pairs (j_1, j_2) such that the particles $(1, 2), (3, 4), \dots, (n_p - 1, n_p)$ are partners. Given a specified residence time, τ_r , the inflow and outflow events consist of randomly selecting n_{in} pairs of particles and exchanging their thermodynamical properties by the properties of a prescribed inflow. The number of particles pairs to input the system is defined as

$$n_{in} \equiv \text{ceil} \left(\frac{1}{2} \frac{\Delta t}{\tau_r} n_p \right), \quad (3.41)$$

where $\text{ceil}(\cdot)$ denotes the ceil function of a real number, i.e., the smallest integer not less than a given real. Given a specified pairwise time, τ_p , the pairing event consists of randomly selecting a number of pairs of particles, different from the inflow particles, equal to

$$n_{pair} \equiv \text{ceil} \left(\frac{1}{2} \frac{\Delta t}{\tau_p} n_p \right), \quad (3.42)$$

for pairing. Then the chosen particles (inflow/outflow and pairing) are randomly shuffled. Between these discrete times, the pairs of particles (j_1, j_2) evolve according to the following mixing law

$$\frac{dh^{(j_1)}}{dt} = -\frac{h^{(j_1)} - h^{(j_2)}}{\tau_m}, \quad (3.43)$$

$$\frac{dh^{(j_2)}}{dt} = -\frac{h^{(j_2)} - h^{(j_1)}}{\tau_m}, \quad (3.44)$$

$$\frac{dp^{(j_1)}}{dt} = 0, \quad (3.45)$$

$$\frac{dp^{(j_2)}}{dt} = 0, \quad (3.46)$$

$$\frac{dY_i^{(j_1)}}{dt} = -\frac{Y_i^{(j_1)} - Y_i^{(j_2)}}{\tau_m} + \frac{\dot{\omega}_i^{(j_1)} W_i}{\rho}, \quad i = 1, \dots, n_s, \quad (3.47)$$

$$\frac{dY_i^{(j_2)}}{dt} = -\frac{Y_i^{(j_2)} - Y_i^{(j_1)}}{\tau_m} + \frac{\dot{\omega}_i^{(j_2)} W_i}{\rho}, \quad i = 1, \dots, n_s. \quad (3.48)$$

and the equation of state, Eq.(3.14).

3.6 The Geometry of Reactive Systems

In this section it is developed a geometric language to interpret a stirred reactor such as PaSR/IEM or PMSR. This approach is based on the theory of dynamical systems and allows one to identify the thermodynamical state of a reactive system as a vector and its evolution as a vector path on the systems phase space.

3.6.1 Composition Space

Given a reactive mixture in a stirred reactor, such as PaSR/IEM or PMSR, its thermodynamical state may be completely determined by the mass fraction Y_i ($i = 1, \dots, n_s$) of the n_s chemical species, the specific enthalpy h and pressure p . The thermodynamic state of the reactive mixture can be represented in a compact way by the *composition* vector defined as

$$\phi \equiv (h, p, Y_1, \dots, Y_{n_s})^T, \quad (3.49)$$

where the superscript T denotes the transposition operation. One should note that, due to the invariance of the system number of atoms, which ensures the total conservation of the mass, the components of vector ϕ are not linearly independent.

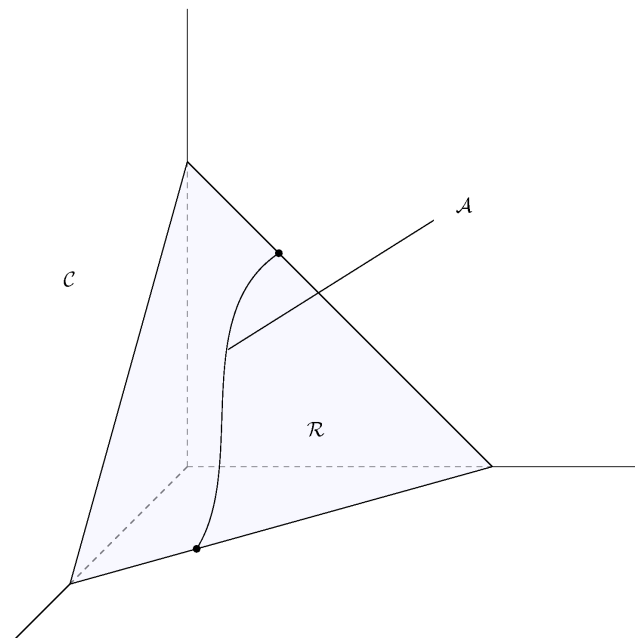


Figure 3.1: Sketch of the composition space and its subsets.

Defining $n_\phi \equiv n_s + 2$, the composition ϕ is a point in the n_ϕ -dimensional Euclidean space the so called *composition space* (\mathcal{C}), where the first direction is associated with the enthalpy, the second with the pressure and the other n_s are related to the chemical species. The region of the composition space defined by all physical realizable values of ϕ — those that respect elemental conservation — is called *realizable region* (\mathcal{R}). The locus in the realizable region defined by all composition ϕ that occurs in a given flow calculation is called *accessed region* (\mathcal{A}). By definition, the accessed region is a subset of the realizable region, which is a subset of the composition space. Figure 3.1 illustrates the structure of the composition space and its subsets.

3.6.2

Mixture Temperature

The composition vector ϕ completely defines the thermodynamical state of a reactive mixture in a partially stirred reactor. Thus, it is possible to determine the mixture temperature from the components of ϕ . Indeed, the mixture enthalpy is a function of the temperature given by

$$h(T) \equiv \sum_{i=1}^{n_s} Y_i h_i(T) \quad (3.50)$$

where the specific enthalpy of the i -th chemical species is given by

$$h_i(T) \equiv h_i^o + \int_{T^o}^T c_{p_i}(T') dT' \quad (3.51)$$

where h_i^o and c_{p_i} respectively are the specific enthalpy of formation and specific heat of i -th chemical species and T^o is the temperature at the standard state. In this work, h_i^o and c_{p_i} are computed using the **Chemkin-II** package by Kee et al. (1989) [37] and the system temperature is obtained from the Eq.(3.51) using the bisection method.

3.6.3

Reaction Mapping

Considering an ideal spatially homogeneous, transient, chemical reactor such as PaSR/IEM or PMSR, the evolution of the composition of each particle in the reactor can be written in a general framework according to the following set of ordinary differential equations

$$\frac{d\phi^{(j)}}{dt} = \mathbf{\Gamma}^{(j)}(t) + \mathbf{S}(\phi^{(j)}, t), \quad (3.52)$$

where $\mathbf{\Gamma}^{(j)}(t)$ is the rate of change due to micromixing transport and $\mathbf{S}(\phi^{(j)}, t)$ is the rate of change associated to the chemical reactions.

Integrating both sides of equation Eq.(3.52) from an initial time t_0 to a time t gives

$$\phi^{(j)}(t) = \phi_0^{(j)} + \int_{t_0}^t \Gamma^{(j)}(t') dt' + \int_{t_0}^t \mathbf{S}(\phi^{(j)}, t') dt', \quad (3.53)$$

and defining the *reaction mapping*

$$\mathbf{R}(\phi_0^{(j)}, t) \equiv \phi^{(j)}(t), \quad (3.54)$$

as the solution of Eq.(3.52) after a time t starting from the initial composition $\phi^{(j)}(t_0) = \phi_0^{(j)}$.

The reaction mapping corresponds to a trajectory in composition space, which, for large values of t , tends to the equilibrium composition for the given enthalpy and pressure on $\phi_0^{(j)}$, such as shown in Figure 3.2.

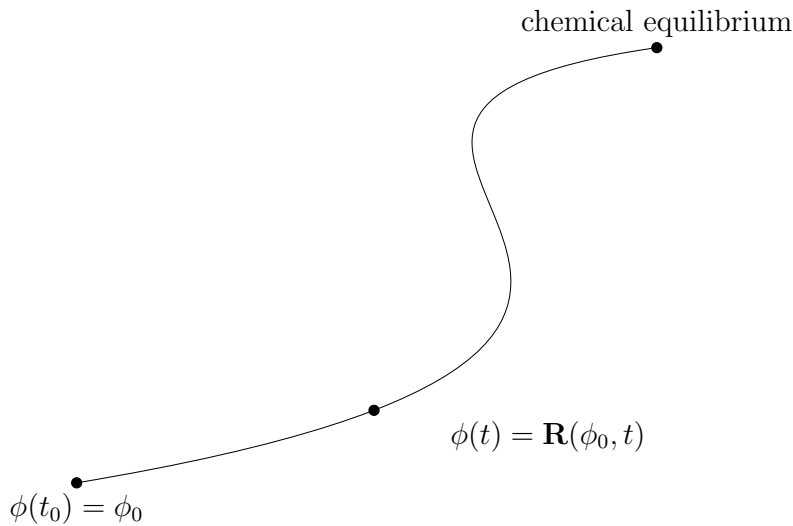


Figure 3.2: Sketch of a trajectory in composition space departing from an initial composition ϕ_0 until the chemical equilibrium.

3.6.4

Reaction Vector

For each particle with composition $\phi^{(j)}$, the reaction vector $\mathbf{S}(\phi^{(j)}, t)$ has its first and second components equal to zero and the next n_s components given by the mass rate of production of each species, i.e.,

$$\mathbf{S}(\phi^{(j)}, t) = \left(0, 0, \frac{\dot{\omega}_1^{(j)} W_1}{\rho}, \dots, \frac{\dot{\omega}_{n_s}^{(j)} W_{n_s}}{\rho} \right)^T. \quad (3.55)$$

3.6.5 Evolution Equations of PaSR/IEM

In the case of the IEM model the mixing vector can be written as

$$\mathbf{\Gamma}^{(j)}(t) = -\frac{1}{\tau_m} \left(h^{(j)} - \langle h \rangle, 0, Y_1^{(j)} - \langle Y_1 \rangle, \dots, Y_{n_s}^{(j)} - \langle Y_{n_s} \rangle \right)^T, \quad (3.56)$$

or, equivalently,

$$\mathbf{\Gamma}^{(j)}(t) = -\frac{\boldsymbol{\phi}^{(j)} - \langle \boldsymbol{\phi} \rangle}{\tau_m}, \quad (3.57)$$

where $\langle \boldsymbol{\phi} \rangle$ is the ensemble average composition vector is given by

$$\langle \boldsymbol{\phi} \rangle = (\langle h \rangle, 0, \langle Y_1 \rangle, \dots, \langle Y_{n_s} \rangle)^T, \quad (3.58)$$

such that the composition of the j -th stochastic particle evolves according to the following system of ODEs

$$\frac{d\boldsymbol{\phi}^{(j)}}{dt} = -\frac{\boldsymbol{\phi}^{(j)} - \langle \boldsymbol{\phi} \rangle}{\tau_m} + \mathbf{S}(\boldsymbol{\phi}^{(j)}, t). \quad (3.59)$$

3.6.6 Evolution Equations of PMSR

In the case of the PMSR the mixing vectors for the pair of particles (j_1, j_2) can be written as

$$\mathbf{\Gamma}^{j_1}(t) = -\frac{1}{\tau_m} \left(h^{(j_1)} - h^{(j_2)}, 0, Y_1^{(j_1)} - Y_1^{(j_2)}, \dots, Y_{n_s}^{(j_1)} - Y_{n_s}^{(j_2)} \right)^T, \quad (3.60)$$

$$\mathbf{\Gamma}^{j_2}(t) = -\frac{1}{\tau_m} \left(h^{(j_2)} - h^{(j_1)}, 0, Y_1^{(j_2)} - Y_1^{(j_1)}, \dots, Y_{n_s}^{(j_2)} - Y_{n_s}^{(j_1)} \right)^T, \quad (3.61)$$

or, equivalently,

$$\mathbf{\Gamma}^{j_1}(t) = -\frac{\boldsymbol{\phi}^{(j_1)} - \boldsymbol{\phi}^{(j_2)}}{\tau_m}, \quad (3.62)$$

$$\mathbf{\Gamma}^{j_2}(t) = -\frac{\boldsymbol{\phi}^{(j_2)} - \boldsymbol{\phi}^{(j_1)}}{\tau_m}, \quad (3.63)$$

such that the compositions of a pair of particles (j_1, j_2) evolves according to the following system of ODEs

$$\frac{d\boldsymbol{\phi}^{(j_1)}}{dt} = -\frac{\boldsymbol{\phi}^{(j_1)} - \boldsymbol{\phi}^{(j_2)}}{\tau_m} + \mathbf{S}(\boldsymbol{\phi}^{(j_1)}, t), \quad (3.64)$$

$$\frac{d\boldsymbol{\phi}^{(j_2)}}{dt} = -\frac{\boldsymbol{\phi}^{(j_2)} - \boldsymbol{\phi}^{(j_1)}}{\tau_m} + \mathbf{S}(\boldsymbol{\phi}^{(j_2)}, t). \quad (3.65)$$