

Chemistry Training Problem Part 1: Presentation

August 2020

CPFD Software
1255 Enclave Parkway, Suite E
Houston, TX 77077 USA
+1 (713) 429-1252
www.cdfd-software.com

Training Plan

Chemistry training will be provided in two parts

- Introduction to the Chemistry module
 - Volume Average Chemistry
 - Discrete Particle Chemistry
 - Stoichiometric Form
 - Species Form
 - Reaction Rate Coefficients
- Chemistry Project
 - Single-Cell Example using Volume Average Chemistry

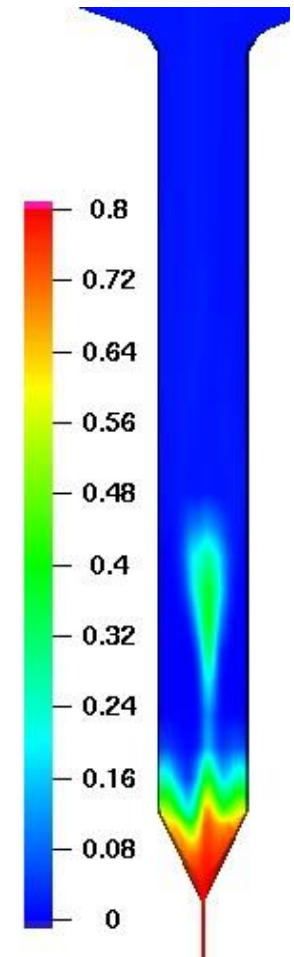
Applications of Chemistry Module

Reaction chemistry is an integral part of many industrial applications

- FCC Reactors and Regenerators
- Circulating Fluidized Bed Combustors
- Biomass and Coal Gasifiers
- Chemical Looping Combustion
- Desulfurization Reactors and Regenerators
- Polysilicon Deposition

Reaction chemistry is used to study

- FBR reaction and conversion efficiency
- Location and severity of reactor hot spots
- Reactant feed locations
- Cooling optimization for exothermic reactions
- Heating optimization for endothermic reactions



Weight fraction of silane
gas in polysilicon
deposition reactor

Barracuda Chemistry Module

The chemistry module adds chemical reactions to particle-fluid simulations

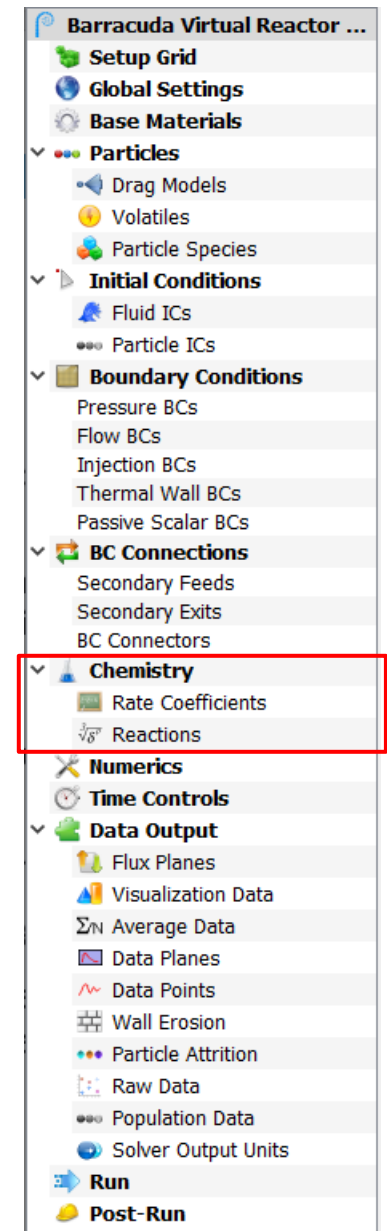
Chemical reactions can affect all aspects of fluidized bed behavior

- Gas flow and composition: Reactions that produce gases from solids
- Particle size and density: Reactions that deposit new solids or consume existing solids
- Temperature: Reactions that produce or consume heat

Conversely, all aspects of fluidized bed behavior affect chemical reactions

- Particle-fluid mixing: Affects reaction rate, conversion
- Thermal mixing: Affects reaction rate, reaction selectivity

Strong coupling between reaction chemistry, particle-fluid dynamics, and thermal dynamics



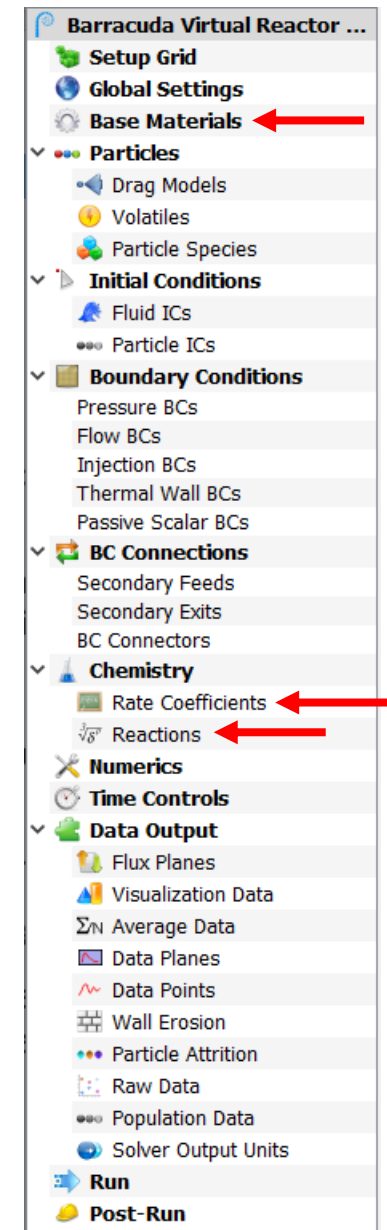
Specifying Chemistry in Barracuda

All reactions and reaction rates are specified in the chemistry module

All participating gases and solid materials must be specified in Base Materials

Reaction chemistry is defined in Barracuda using

- Rate Coefficients: expressions to define rate dependence on temperature, pressure, fluid density, fluid volume fraction, and solids
- Reactions: definitions of reactions and rates



Reaction Chemistry Basics

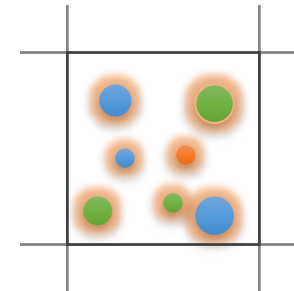
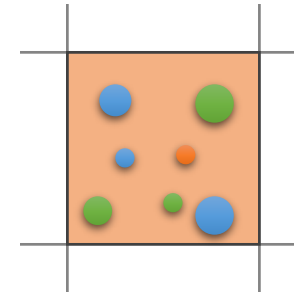
Many different types of reactions available:

- Homogeneous: Reaction between fluids in the fluid phase. Doesn't involve solids.
- Heterogeneous: Reaction involving solids as reactant, product and/or catalyst
 - Deposition: Fluid phase deposits material on solid surface
 - Consumption: Solid material is consumed to form fluid
 - Catalytic: Fluids react to form other fluids on solid surface
 - Solids-to-solids: Solid material reacts to form other solid material

Reaction Chemistry in Barracuda

There are two ways reaction chemistry can be specified and solved in Barracuda Virtual Reactor

- Volume Averaged Chemistry: The gas volume in each computational cell acts as a control volume for reaction calculations
- Discrete Particle Chemistry: Each cloud is given a separate control volume for reaction rate calculations



Volume Average versus Discrete Particle Chemistry

Volume average chemistry

- Gas phase reactions
- Catalytic reactions
- May be used for solid consumption and deposition reactions, but not recommended if particle properties vary within the cell

Discrete particle chemistry

- Only available for reactions where a solid is consumed or produced
- Highly recommended for reactions where solids react to form other solids
- Typically higher accuracy but results in slightly slower computation

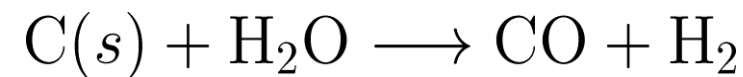
Volume Average Chemistry

Specifying Reactions in Barracuda

Reactions are written in two ways in Barracuda:

- Stoichiometric
- Species

The forward steam gasification reaction is used to demonstrate. In the Stoichiometric approach, this reaction is:

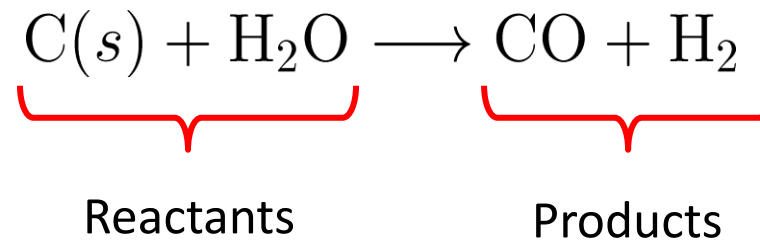


and the rate of this reaction is:

$$r_{\text{forward}} = \frac{d[\text{CO}]}{dt} = \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}]$$

Stoichiometric Reactions

In the Stoichiometric approach, the reaction is specified by a balanced equation showing the reactants and products:



Reactants are consumed and products are produced at the specified reaction rate:

$$r_{\text{forward}} = \frac{d[\text{CO}]}{dt} = \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}]$$

Species Reactions

With the species form, the reaction rate for each species is explicitly written:

$$\left. \begin{aligned} \frac{d[\text{CO}]}{dt} &= \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}] \\ \frac{d[\text{H}_2]}{dt} &= \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}] \end{aligned} \right\} \text{Positive rate: Products}$$

$$\left. \begin{aligned} \frac{d[\text{H}_2\text{O}]}{dt} &= - \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}] \\ \frac{d[\text{C}]}{dt} &= - \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \exp \left(\frac{-22645\text{K}}{T} \right) \rho_{\text{C}} [\text{H}_2\text{O}] \end{aligned} \right\} \text{Negative rate: Reactants}$$

Rate Coefficients as Building Blocks

Temperature, pressure, and solids dependence are often reused many times.

In Barracuda, these terms are entered as a rate coefficient, which can be in any number of reaction rate expressions:

$$r_{\text{forward}} = \frac{d[\text{CO}]}{dt} = \underbrace{\left(219 \frac{\text{m}^3}{\text{kg K s}}\right) T \exp\left(\frac{-22645\text{K}}{T}\right) \rho_{\text{C}} [\text{H}_2\text{O}]}_{\text{Rate Coefficient, } k_0}$$

In Species form, the reactions become:

$$\begin{aligned} \frac{d[\text{CO}]}{dt} &= k_0 [\text{H}_2\text{O}] & \frac{d[\text{H}_2]}{dt} &= k_0 [\text{H}_2\text{O}] \\ \frac{d[\text{C}]}{dt} &= -k_0 [\text{H}_2\text{O}] & \frac{d[\text{H}_2\text{O}]}{dt} &= -k_0 [\text{H}_2\text{O}] \end{aligned}$$

where: $k_0 = \left(219 \frac{\text{m}^3}{\text{kg K s}}\right) T \exp\left(\frac{-22645\text{K}}{T}\right) \rho_{\text{C}}$

General Rate Coefficient Forms

There are multiple forms of the rate coefficient available in Barracuda to accommodate the wide range of possible reaction dependencies

- Arrhenius form
- Polynomial form
- Table-Based
- Catalyst Deactivation
- User-defined Expression

$$k = c_0 T^{c_1} P^{c_2} \rho_f^{c_3} \theta_f^{c_4} \exp\left(-\frac{E}{T} + E_0\right) [\text{solids terms}]$$

$$k = (c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4) [\text{solids terms}]$$

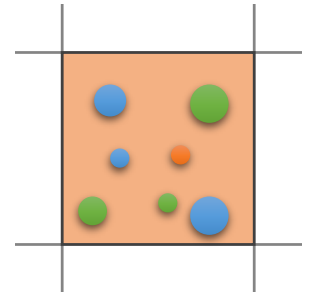
$$\varphi = \frac{B_c + 1}{B_c + \exp(A_c C_{ci})}$$

Volume Average Chemistry Arrhenius Rate Coefficient

$$k = c_0 T^{c_1} P^{c_2} \rho_f^{c_3} \theta_f^{c_4} \exp \left(-\frac{E}{T} + E_0 \right) [\text{solids terms}]$$

Diagram illustrating the components of the Volume Average Chemistry Arrhenius Rate Coefficient equation:

- c_0 : Constant
- T^{c_1} : Temperature
- P^{c_2} : Pressure
- $\rho_f^{c_3}$: Fluid Density
- $\theta_f^{c_4}$: Fluid Volume Fraction
- $\exp \left(-\frac{E}{T} + E_0 \right)$: Activation Energy
- [solids terms]: Solids terms



Solid terms can be specified for all solids or individual solids species:

- Mass of solids / cell volume
- Surface area solids / cell volume
- Mean diameter of solids
- Volume of solids / cell volume (volume fraction)

General Reaction Rate Forms

Power Law: $R = C_0 k_0 [G_1]^\alpha [G_2]^\beta + C_1 k_1 [G_3]^\gamma \dots$

LH Mode (Langmuir-Hinshelwood):
$$R = \frac{C_0 k_0 [G_1]^\alpha [G_2]^\beta + C_1 k_1 [G_3]^\gamma \dots}{1 + k_2 [G_4]^\delta [G_5]^\varepsilon + k_3 [G_6]^\zeta \dots}$$

where:

- C_i is a constant
- k_i is a rate coefficient
- $[G_i]$ is a gas concentration

The Control Volume

The reaction rate is multiplied by a control volume to calculate the mass or mole rate of change.

Possible control volumes are:

- In experiments:
 - Entire reactor volume: gas + particles
 - Gas volume in reactor: gas only
 - Volume, mass, or surface area of particles
- In a CFD model:
 - The volume of a cell or the gas volume in the cell (Eulerian)
 - The volume of particles (Lagrangian)

In Barracuda's Volume Average chemistry, the control volume is the gas volume in a cell.

Check the volume basis of new reactions carefully to ensure consistency.

Discrete Particle Chemistry

When to Use Discrete Particle Chemistry

Available / Recommended

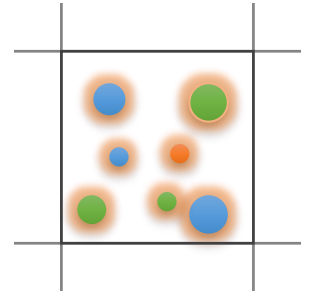
- Is only available for reactions where a solid species is consumed or produced
- Recommended for reactions where solids react to form other solids. It is technically permissible to do this on a volume-averaged basis, but results can be quite poor.
- Recommended when there are large temperature differences between particles and fluids
- Recommended for cases with widely varying particle properties within the same cell (i.e. size variation, composition variation, etc.)

Typically gives higher accuracy than volume-averaged chemistry, but results in slightly slower computation

Requires specification of reaction rates in species form

No reaction will occur in a computational cell unless particles are present

Discrete Particle Chemistry Basics



Reaction rates are calculated for each cloud.

Reaction rate units in discrete particle chemistry do not have a volume basis.

- Reaction rate units: mol/s, kmol/s, kg/s, g/s, and mol/min

Solid terms in discrete particle rate coefficients are based on each particle:

- Particle mass units: kg, g, lb
- Particle surface area units: m^2 , cm^2 , ft^2 , in^2
- Particle diameter units: m, cm, micron, ft, in

Eulerian terms in reaction rate expressions and rate coefficients (gas concentration, pressure, etc.) are cell values.

Temperature is weighted between the individual particle temperature and the cell fluid temperature.

Solids Terms in Discrete Particle Chemistry

In discrete particle chemistry, each particle has a separate control volume:

$$v_{cp} = V_{cell} / N_p$$

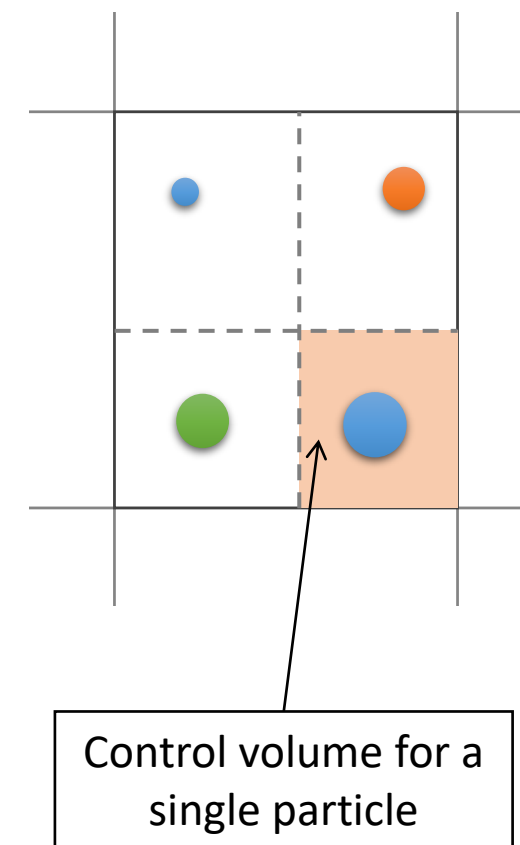
Individual particle control volume Cell Volume Number of particles in the cell

The particle reaction rate, r_p : $r_p = r\theta_f v_{cp} = r\theta_f (V_{cell} / N_p)$

Where:

- r = user-specified reaction rate
- V_{cp} = particle control volume
- θ_f = fluid volume fraction

The total reaction rate in the cell is the sum of all particle reaction rates

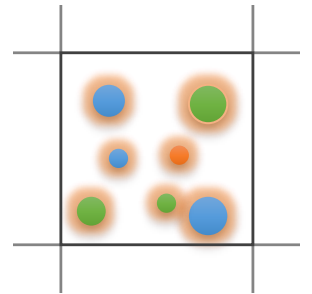


Discrete Particle Chemistry Rate Coefficient

$$k = c_0 T^{c_1} P^{c_2} \rho_f^{c_3} \theta_f^{c_4} (N_p/V)^{c_5} \exp\left(-\frac{E}{T} + E_0\right) [\text{solids terms}]$$

Diagram illustrating the rate coefficient equation with parameter labels:

- c_0 : Constant (blue arrow pointing down)
- T^{c_1} : Temperature (blue arrow pointing up)
- P^{c_2} : Pressure (blue arrow pointing down)
- $\rho_f^{c_3}$: Fluid Density (blue arrow pointing up)
- $\theta_f^{c_4}$: Fluid Volume Fraction (red arrow pointing down)
- $(N_p/V)^{c_5}$: # particle / cell volume (red arrow pointing up)
- $\exp\left(-\frac{E}{T} + E_0\right)$: Activation Energy (blue arrow pointing down)



Solids terms can be specified for all solids or individual solids species:

- Mass of particle or mass of species in particle
- Surface area
- Diameter
- Volume fraction

Specifying Reactions in Discrete Particle Chemistry

Reactions are specified in discrete particle chemistry using the species form

- Main reaction rate is always based on a solid species

$$\frac{d[C(s)]}{dt} = - \left(219 \frac{\text{m}^3}{\text{kg K s}} \right) T \theta_f \exp \left(\frac{-22645\text{K}}{T} \right) m_C [H_2O] \quad \leftarrow \text{Reactant}$$

Negative rate because C(s) is being consumed

- Participating reaction rates are based on the main solid species reaction rate

$$\begin{aligned} \frac{d[H_2O]}{dt} &= 1 \frac{d[C(s)]}{dt} \quad \leftarrow \text{Reactant} \\ \frac{d[H_2]}{dt} &= -1 \frac{d[C(s)]}{dt} \\ \frac{d[CO]}{dt} &= -1 \frac{d[C(s)]}{dt} \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Products}$$

“Negative of a negative”, so CO is being produced

Summary

The chemistry module couples chemical reactions with thermal and particle-fluid dynamics

The temperature, pressure, density, and solids dependence of a reaction is stored in the rate coefficient

Barracuda has two options for reaction control volume:

- Volume Average chemistry (gas volume of a cell = control volume)
 - Reaction rates can be written in stoichiometric or species form
- Discrete Particle chemistry (each particle has a separate control volume)
 - Reactions are specified in species form
 - The rate must be defined in terms of a solid species