Chemistry Lecture

February 2018

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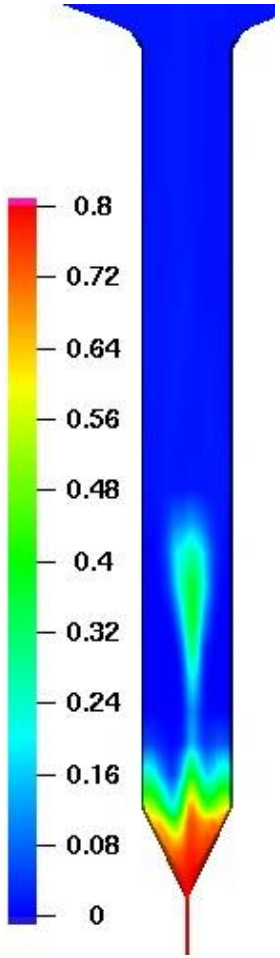
Training Plan

- Chemistry training will be provided in three parts
  - Lecture: Introduction to the Chemistry module
    - Volume Average Chemistry
    - Discrete Particle Chemistry
  - Example 1: Set up of training problem using Volume Average Chemistry
  - Example 2: Set up of training problem using Discrete Particle Chemistry

Training Objectives

- Introduction to chemistry module
- Reaction Chemistry Basics
- Chemistry concepts in Barracuda
  - Volume Average Chemistry
  - Discrete Particle Chemistry
  - Stoichiometric Form
  - Species Form
  - Reaction Rate Coefficients

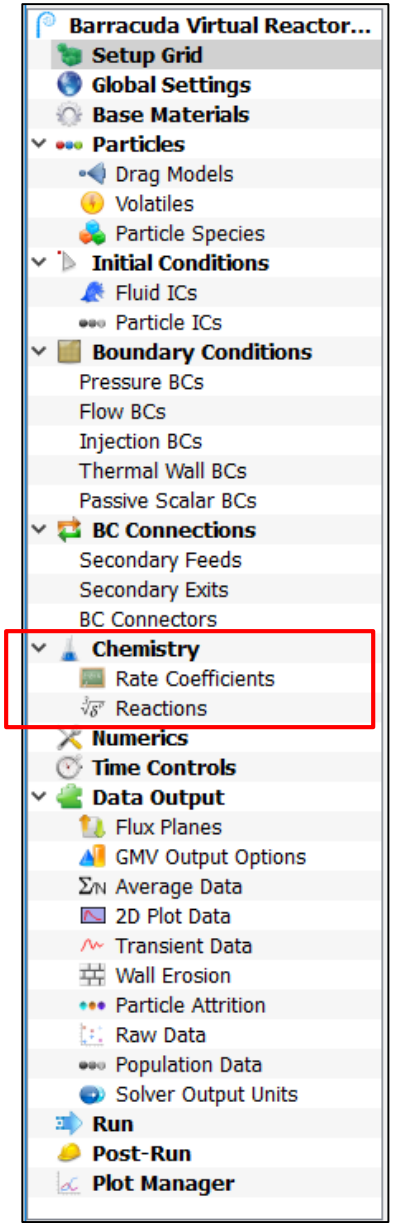
Applications of Chemistry Module



Weight fraction of silane gas in polysilicon deposition reactor

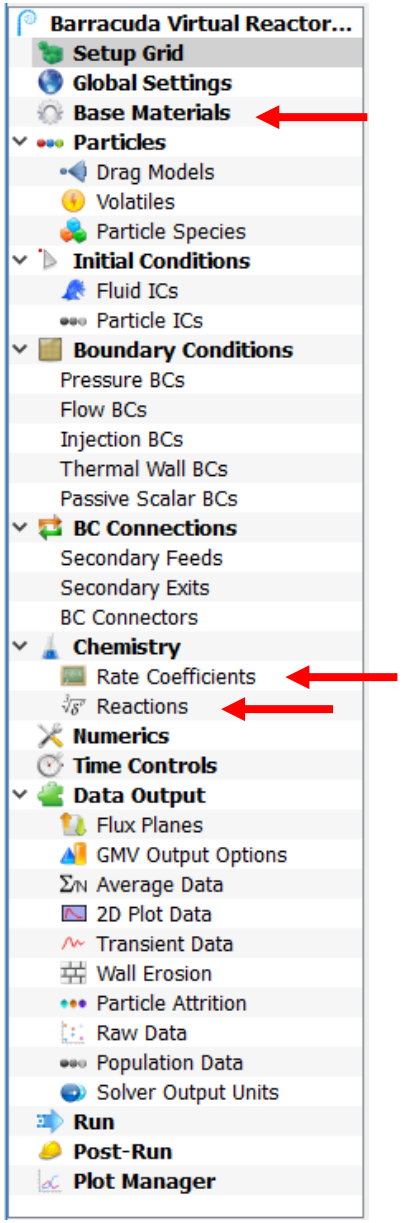
- Reaction chemistry is an integral part of many industrial applications
  - FCC Reactors and Regenerators
  - Circulating Fluidized Bed Combustors
  - Biomass and Coal Gasifiers
  - Chemical Looping Combustion
  - Desulfurization Reactors and Regenerators
  - Polysilicon Deposition
- Reaction chemistry 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

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 the **Base Materials**
- Reaction chemistry is defined in Barracuda using
  - **Rate Coefficients:** specifies expressions to define rate dependence on temperature, pressure, fluid density, fluid volume fraction, and solids
  - **Reactions**: defines the reactions and rates

Reaction Chemistry Basics

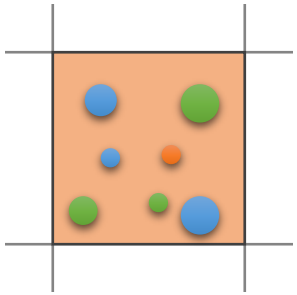
Many different types of reactions available:

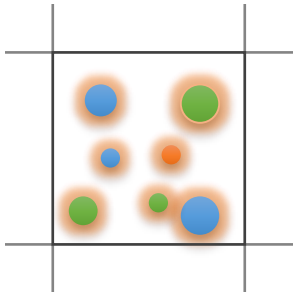
- **Homogeneous:** Reaction between fluids in the fluid phase. Doesn't involve solids.
- **Heterogeneous:** Reaction involving solids as reactant, product and/or catalyst
  - **Deposition:** Fluid phase deposits material on solid surface
  - **Consumption:** Solid material is consumed to form fluid
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

- **Volume Averaged Chemistry:** The gas volume in each cell in the grid acts as a control volume for reaction calculations
- **Discrete Particle Chemistry:** Each computational particle 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

$$\mathrm{C}(s) + \mathrm{H_2O} \longrightarrow \mathrm{CO} + \mathrm{H_2}$$

and the rate of this reaction is

$$r_{\text{forward}} = \frac{d[\mathrm{CO}]}{dt} = \left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

The chemical kinetics shown are for demonstration or education purpose only and have not been validated, nor are they recommended for any application. Development, validation, and use of chemical kinetics is the User's responsibility, and CPFD Software, LLC, does not warrant or endorse these chemical kinetics for any purpose.

Stoichiometric Reactions

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

$$\underbrace{\mathrm{C}(s) + \mathrm{H_2O}}_{\textbf{Reactants}} \longrightarrow \underbrace{\mathrm{CO} + \mathrm{H_2}}_{\textbf{Products}}$$

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

$$r_{\text{forward}} = \frac{d[\mathrm{CO}]}{dt} = \left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

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Species Reactions

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

$$\frac{d\,[\mathrm{CO}]}{dt} = \left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

$$\frac{d\,[\mathrm{H_2}]}{dt} = \left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

Positive rate: Products

$$\frac{d\,[\mathrm{H_2O}]}{dt} = -\left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

$$\frac{d\,[\mathrm{C}]}{dt} = -\left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}}\,[\mathrm{H_2O}]$$

Negative rate: Reactants

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Reaction Rate Functionality

- Reactions are often a function of
  - Gas species concentrations: $[H_2O]$, $[H_2]$, $[CO]$
  - Solid concentrations: ρ_S, ρ_C
  - Solid surface area, diameter, volume: A_S, d_S, θ_S
  - Fluid and solid temperature: T
  - Gas pressure, P
  - Gas density, ρ_f

Example: $$r = \left(219 \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T \exp\left(\frac{-22645\mathrm{K}}{T}\right) \rho_{\mathrm{C}} [\mathrm{H_2O}]$$

- In a fluidized bed reactor, these values can vary dramatically with time and position.
  - Barracuda simulations are transient
  - The computational grid provides spatial resolution

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Rate Coefficient

- 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

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

- In Species form, the reactions become

$$\frac{d[\text{CO}]}{dt} = k_0 [\text{H}_2\text{O}] \qquad \frac{d[\text{H}_2]}{dt} = k_0 [\text{H}_2\text{O}]$$
$$\frac{d[\text{C}]}{dt} = -k_0 [\text{H}_2\text{O}] \qquad \frac{d[\text{H}_2\text{O}]}{dt} = -k_0 [\text{H}_2\text{O}]$$

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

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General Rate Coefficient Forms

- There are four forms of the rate coefficient available in Barracuda to accommodate the wide range of possible reaction dependencies
  - **Arrhenius form**

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

  - **Polynomial form**

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

  - **Table-Based**
  - **Catalyst Deactivation**

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

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Volume Average Chemistry Arrhenius Rate Coefficient

Constant

Pressure

Fluid Volume Fraction

Activation Energy

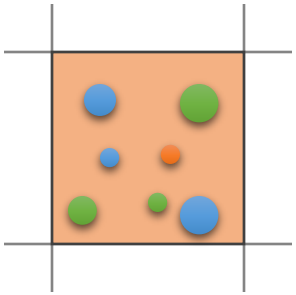
$$k = c_0 T^{c_1} P^{c_2} \rho_f{}^{c_3} \theta_f{}^{c_4} \exp\left(-\frac{E}{T} + E_0\right) [\text{solids terms}]$$

Temperature

Fluid Density

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)*



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General Reaction Rate Forms

- Power Law

$$R = C_0 k_0 \left[G_1\right]^{\alpha} \left[G_2\right]^{\beta} + C_1 k_1 \left[G_3\right]^{\gamma} \ldots$$

- LH Mode (Langmuir-Hinshelwood)

$$R = \frac{C_0 k_0 \left[G_1\right]^{\alpha} \left[G_2\right]^{\beta} + C_1 k_1 \left[G_3\right]^{\gamma} \ldots}{1 + k_2 \left[G_4\right]^{\delta} \left[G_5\right]^{\varepsilon} + k_3 \left[G_6\right]^{\zeta} \ldots}$$

where

C_i is a constant

k_i is a rate coefficient

$[G_i]$ is a gas concentration

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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 Volume Average chemistry, the control volume is the gas volume in a cell
- Often in literature, a reaction rate will be specified based on the entire reactor volume (gas + particles). **Check the volume basis of new reactions carefully.**

CPU Parallel

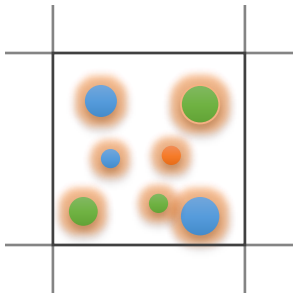
- Volume-average chemical reaction calculations can be performed in parallel on the CPU
- Calculation speed can be significantly faster using CPU Parallel
- CPU Parallel requires a Parallel license
- By default, the Barracuda Virtual Reactor GUI will detect number of CPU cores available, and use the that number of cores minus one for CPU Parallel calculations
- When running multiple simulations, leave 1 CPU core unused
  - This will help to keep the system responsive

Discrete Particle Chemistry

When to Use Discrete Particle Chemistry

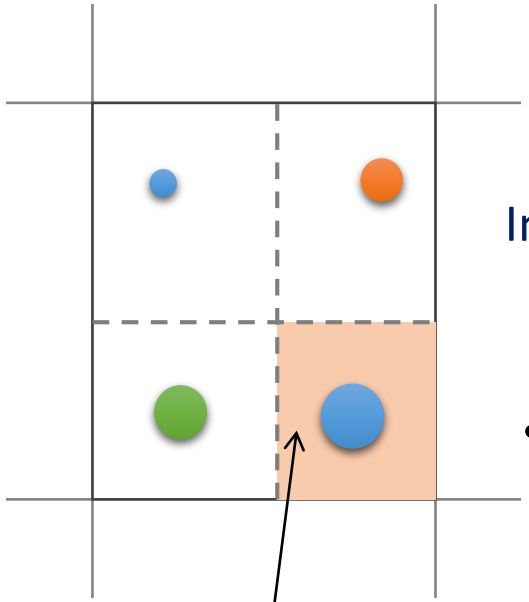
- Is only available for reactions where a solid species is consumed or produced
- Should be used for reactions where solids react to form other solids. It is technically permissible to do this on a volume-averaged basis, but results can be quite poor.
- Is recommended when there are large temperature differences between particles and fluids
- Is 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
- Currently requires conversion of reaction rates into a discrete particle form
- No reaction will occur in a computational cell unless particles are present

Discrete Particle Chemistry Basics



- Reaction rates are calculated for each computational particle
- Reaction rate units in discrete particle chemistry do not have a volume basis. **Reaction rate** units are 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



Control volume for a single particle

- 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, is the user-specified reaction rate, r, multiplied by the particle control volume, v_{cp}, and the fluid volume fraction, θ_f:

$$r_p = r\theta_f v_{cp} = r\theta_f \left(V_{cell}/N_p\right)$$

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

Discrete Particle Chemistry Rate Coefficient

Constant

Pressure

Fluid Volume Fraction

Activation Energy

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

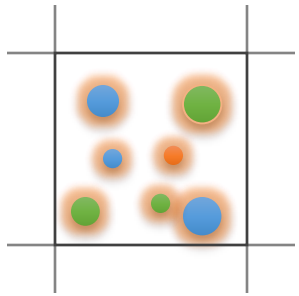
Temperature

Fluid Density

particle / cell volume

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



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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

$$\frac{d[\mathrm{C}(s)]}{dt} = -\left(219\ \frac{\mathrm{m}^3}{\mathrm{kg\,K\,s}}\right) T\theta_f \exp\left(\frac{-22645\mathrm{K}}{T}\right) m_{\mathrm{C}}\,[\mathrm{H_2O}]$$

← **Reactant**

Negative rate → C(s) is being consumed

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

$$\frac{d[\mathrm{H_2O}]}{dt} = 1\ \frac{d[\mathrm{C}(s)]}{dt}$$

← **Reactant**

$$\frac{d[\mathrm{H_2}]}{dt} = -1\ \frac{d[\mathrm{C}(s)]}{dt}$$

$$\frac{d[\mathrm{CO}]}{dt} = -1\ \frac{d[\mathrm{C}(s)]}{dt}$$

Products

"Negative of a negative" → CO is being produced

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Lecture Summary

- The chemistry module couples chemical reactions with thermal and particle-fluid dynamics
- The temperature, pressure, density, 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 for discrete particle chemistry in a **species** form. The rate must be a function of a solid species reaction.