Reactor Analysis
Types of Reactors

Most of the process simulators provide four kinds of reactor models, including: (1) a stoichiometric model that permits the specification of reactant conversions and extents of reaction for one or more reactions, (2) a kinetic model for a continuous stirred-tank reactor (CSTR), for homogeneous phases (vapor and liquid) and assuming perfect mixing, (3) a kinetic model for a tubular reactor in plug flow (PFTR), for homogeneous phases (vapor and liquid) and assuming no backmixing (dispersion), and (4) a model for multiple phases (vapor, liquid, and solid) in chemical equilibrium, where the approach to equilibrium for individual reactions can be specified.
Stoichiometric Reactor Module

Using the fractional conversion of a key reactant or the extent of reaction, the RSTOIC model determines the flow rates of all of the species leaving the reactor. The RSTOIC model also includes the energy balance and determines either the rate of heat transfer, to or from the reactor, or the temperature of the product stream.

The flowsheet schematic for the subroutine is:

```
MATERIAL (any number)  
                      ---
                      v
                      RSTOIC
                      ^
                      |  WATER (optional)
                      |  --------------------
                      |                      
                      |  HEAT (optional)  
```

HEAT (optional)
In these models, the fractional conversion, $X$ of key reactant $k$,

$$X_k = \frac{n_{k_{in}} - n_{k_{out}}}{n_{k_{in}}} = \frac{\Delta n_k}{n_{k_{in}}}$$

where $n_{kin}$ and $n_{kout}$ are moles of species $k$ entering and leaving the reactor and $0 \leq X_k \leq 1$, or the extent of reaction $i$, are specified.

$$\xi_i = \frac{\Delta n_{ji}}{v_{ji}} \quad j = 1, \ldots, C$$
Then, using those stoichiometric equations, the models determine the flow rates of all species leaving the reactor. Many of the models also include the energy balance and determine either the rate of heat transfer, to or from the reactor, or the temperature of the product stream.
Stoichiometric Reactors (3)

Consider the catalytic oxidation of ethanol. A very dilute stream containing ethanol and oxygen is heated over a catalyst bed, and ethanol is oxidized to acetaldehyde, which is in turn oxidized to carbon dioxide:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \quad + \quad \frac{1}{2}\text{O}_2 \quad \rightarrow \quad \text{CH}_3\text{COH} & \quad + \quad \text{H}_2\text{O} \\
\text{CH}_3\text{COH} & \quad + \quad \frac{5}{2}\text{O}_2 \quad \rightarrow \quad \text{CO}_2 & \quad + \quad 2\text{H}_2\text{O}
\end{align*}
\]

The conversion of ethanol is approximately 95%, and the conversion of acetaldehyde formed by the first reaction is approximately 88%. This reaction can be simulated using a stoichiometric reactor model. The specifications are as shown below:

- **Flowrate**: 100 kmol/hr
- **Component** | **Vol. frac**
  - Nitrogen: 0.988
  - Oxygen: 0.010
  - Ethanol: 0.001
- **Temp**: 595 K
- **Press**: 1 atm

[Diagram of reactor process]
Equilibrium Reactors

Most simulators provide two models for calculating chemical equilibrium. In addition, simultaneous phase equilibrium can also be requested. The first type of model is based on the use of chemical equilibrium constants for specified stoichiometric reactions. The second model is based on the minimization of Gibbs free energy. The reactions are not specified, but the possible products are. An independent set of reactions is determined by the model from the stoichiometric reactions.
Gibbs Reactor

The RGIBBS subroutine calculates multi-phase chemical equilibrium involving a vapor phase, multiple liquid phases, and pure solid phases. There is no need to specify the stoichiometry for an independent set of chemical reactions because RGIBBS minimizes the Gibbs free energy subject to mass-balance constraints. It is, however, possible to specify stoichiometry when it is desirable to specify the approach of one or more reactions to chemical equilibrium.
Shown here is the flowsheet connectivity for the RGIBBS subroutine. Any number of product streams can be specified, since RGIBBS can calculate phase equilibrium for any number of product phases. Also, heat streams can be used.
Equilibrium Reactor

The REQUIL subroutine calculates chemical equilibrium and chemical and phase equilibrium involving vapor and liquid phases. Pure solid species may participate in the reactions, but are not taken to be in phase equilibrium. It is also possible to specify an approach to chemical equilibrium for one or more of the reactions.

REQUIL uses chemical equilibrium constants for specified stoichiometric reactions. It solves the mass-action equations for chemical equilibrium.
REquil Module

Shown here is the flowsheet schematic for the REQUAL subroutine. Note that, unlike the RGIBBS model, which can have any number of product streams, only one liquid and one vapor stream are allowed.
Consider the hydrodealkylation reactor shown here. The reactions that take place in the vessel are:

\[
\begin{align*}
C_7H_8 + H_2 & \rightarrow C_6H_6 + CH_4 \\
2C_6H_6 & \rightarrow C_{12}H_{10} + H_2
\end{align*}
\]

The conversion of toluene is 75%, and the conversion of biphenyl (including that produced by the main reaction) is 2%. Adiabatic operation with a 5 psi pressure drop across the reactor is also assumed.

<table>
<thead>
<tr>
<th>Component</th>
<th>lbmol/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>2045.9</td>
</tr>
<tr>
<td>Methane</td>
<td>3020.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>46.2</td>
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<tr>
<td>Toluene</td>
<td>362.0</td>
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<tr>
<td>Biphenyl</td>
<td>1.0</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>5475.9</strong></td>
</tr>
</tbody>
</table>
Results of Equilibrium Calculations (1)

As can be seen, the two models do not give identical outputs. Since RGIBBS generates a complete set of independent reactions from the allowed products, this must mean that a complete set of independent reactions was not specified for the REQUIL unit.

Results of Reactor Simulations

<table>
<thead>
<tr>
<th>Effluent Conditions</th>
<th>REQUIL</th>
<th>RGIBBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °F</td>
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<td>1,627.5</td>
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<tr>
<td>Flow rates, lbmol/hr:</td>
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<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1,700.3</td>
<td>586.0</td>
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<tr>
<td>Methane</td>
<td>3,376.9</td>
<td>4,115.4</td>
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<tr>
<td>Benzene</td>
<td>381.3</td>
<td>213.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.9</td>
<td>32.7</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>11.5</td>
<td>18.4</td>
</tr>
<tr>
<td>Total</td>
<td>5,475.9</td>
<td>4,965.6</td>
</tr>
</tbody>
</table>
Results of Reactor Simulations

<table>
<thead>
<tr>
<th>Effluent Conditions</th>
<th>REQUIL (2 Rxns)</th>
<th>RGIBBS</th>
<th>REQUIL (3 Rxns)</th>
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<tbody>
<tr>
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<td>Flow rates, lbmol/hr:</td>
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<tr>
<td>Hydrogen</td>
<td>1,700.3</td>
<td>586.0</td>
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<tr>
<td>Total</td>
<td>5,475.9</td>
<td>4,965.6</td>
<td>4,965.6</td>
</tr>
</tbody>
</table>
Comments on Equilibrium Reactors

Thus, for cases in which the reactions that take place are known, REQUIL is a better choice for determining equilibrium conditions.

REQUIL computes the same results as RGIBBS when any three independent reactions are specified. In general, the number of independent chemical reactions, $R$, is $C - \rho$, where $C$ is the number of chemical species and $\rho$ is the rank of the atom matrix.
Kinetic Reactors

Steady-state simulation programs contain at least two kinetic reactor models: one for the plug-flow tubular reactor (PFTR or PFR) and one for the continuous-stirred-tank reactor (CSTR or CFSTR). Both models require the user to provide rate equations for the chemical reactions. The model can be used for either of two modes: (1) to compute the reactor volume for a specific conversion, or (2) to compute the conversion for a specified reactor volume.
RPLUG Module

The schematic for the simulation flowsheet is:

MATERIAL
COOLANT (optional)

RPLUG

MATERIAL
COOLANT (optional)

HEAT (optional)

Note that the HEAT stream is used when a COOLANT stream is not specified for the reactor.
PFTR Reactors (1)

A PFTR model is a cylindrical reactor in which conditions vary one-dimensionally in the axial (flow) direction. Axial dispersion is neglected. Thus, there are no radial gradients of temperature, composition, or pressure; and mass transfer by diffusion does not occur in the axial direction. Operation of the reactor can be adiabatic, isothermal, or nonadiabatic, nonisothermal. For the latter, heat transfer to or from the reacting mixture occurs along the length of the reactor.
The RPLUG subroutine is a rigorous one-dimensional, plug flow model that neglects axial dispersion. Thus, there are no radial gradients of temperature, composition, or pressure; and mass transfer by diffusion does not occur in the axial direction. Operation of the reactor can be adiabatic, isothermal, or nonadiabatic, nonisothermal. For the latter, heat transfer to or from the reacting mixture occurs along the length of the reactor. To use RPLUG, it is necessary to specify kinetic rate expressions for each of the chemical reactions.
CSTR Reactors

The CSTR model assumes perfect mixing, and hence, the effluent composition and temperature are taken to be identical to the composition and temperature in the reactor. Most simulators require that the user specify the reactions taking place, and that the volume be given. To compute the reactor volume for a specified conversion, a design specification needs to be made.
The flowsheet schematic for the RCSTR subroutine is:

- MATERIAL (any number) → RCSTR → MATERIAL
- HEAT (optional) → RCSTR → HEAT (optional)
The RCSTR subroutine assumes perfect mixing, and hence, the effluent composition and temperature are taken to be identical to the composition and temperature of the reactor. To use RCSTR, it is necessary to specify kinetic rate expressions for each of the chemical reactions.
CSTR (2)

A difficulty is sometimes encountered when using a CSTR model under adiabatic conditions. Instead of one steady-state solution, multiple steady states may exist, with only some being stable. For example, three steady-state solutions may exist; one stable solution with a high conversion, one stable solution with a low conversion, and one unstable solution with an intermediate conversion. Unfortunately, the CSTR models in simulation programs seek only one solution, and it may not be the desirable high-conversion, stable solution.
ChemCAD

Reactor Simulation
ChemCAD Reactors

• Types of Reactors
• General Considerations and Phase Key
• Stoichiometric Reactor
• Equilibrium Reactor
• Kinetic Reactor
• Gibbs Reactor
Types of Reactor

• Stoichiometric Reactor
• Kinetic Reactor
• Equilibrium Reactor
• Gibbs Reactor
ChemCAD Reactors

General Considerations

Heat of reaction calculated or specified

Reactor thermal mode:
  - Adiabatic
  - Isothermal
  - Heat Load
  - Fixed Temp. profile
  - Utility Stream

Phase Consideration
Stoichiometric Reactor

◎ General
  One Reaction Only
  Conversion must be specified
  Heat of reaction calculated or specified

◎ Typical Uses
  Early of "Budget" process analysis
  Component switching - Changing properties
  Complete reactions or known conditions
Workshop Reactor 1: Stoichiometric Reactor

◎ Benzene + 3 $\text{H}_2$ ---$\rightarrow$ Cyclohexane
◎ Adiabatic
◎ Conversion of 1 mole of benzene to cyclohexane using excess of hydrogen
◎ Change reactor type to isothermal at 600 F.
   Note cooling load required
◎ Highly exothermic reactions will usually require quenching, cooling or multiple reactors.
◎ Cyclohexane is normally produced in multiple reactors with intercooling.
Kinetic Reactor

○ Reactor Type
  CSTR
  Plug Flow

○ Calc Mode
  Volume specified
  Conversion specified

○ Phase
  Liquid (Default)
  Vapor
  Mixed phase, reaction occurs in the liquid phase
  Mixed phase, reaction occurs in the vapor phase
Kinetic Reactor

\[ r_i = \sum_{j=1}^{nrx} N_{ij} A_j e^{-E_j/(RT)} \prod_{k=1}^{nj} (C_{kj})^{a_{kj}} \left( 1 + \sum_{k=1}^{nj} \phi_{kj} e^{-E_j/(RT)} C_k^{b_{kj}} \right)^{-\beta_i} \]

Rate of reaction = \frac{(kinetic term) \times (driving forces)}{(resistance terms)}

- \( r_i \): Rate of formation for component \( i \), mole/volume-time
- \( i \): Subscript for component \( i \)
- \( k \): Subscript for reactant \( k \)
- \( j \): Subscript for reaction \( j \)
- \( N_{ij} \): Stoichiometric coefficient for component \( i \)
- \( A \): Frequency factor (Arrhenius parameter)
- \( E \): Activation energy
- \( R \): Universal gas constant
- \( T \): Absolute temperature
- \( C_{kj} \): Concentration of reactant \( k \), mole/volume or the partial pressure of reactant \( k \)
- \( a_{kj} \): Exponential factor for reactant \( k \) in reaction \( j \)
- \( n \): Number of reactants
- \( nrx \): Number of reaction
- \( \phi_{kj} \): Absorption frequency factor for component \( k \)
- \( \beta_i \): Absorption energy factor for component \( k \)
- \( \beta_i \): Power factor for absorption sites term for reaction, \( j \)
- \( \Sigma \): Product of all reaction concentration terms
- \( \Sigma \): Sum of absorption factor for each reactant
- \( b_{kj} \): Exponential factor for reactant \( k \) in reaction \( j \)
Workshop Reactor2: Kinetic Reactor

Adiabatic kinetic reaction of a lbmole each of acetic acid and ethanol, fed at its bubble point to a 1 liter reactor. Kinetics of the forward and reverse reactions are considered. Mixed phase, reaction occurs in the liquid phase.

Acetic Acid + Ethanol $\leftrightarrow$ Ethyl Acetate + H$_2$O

$r_1 = K_1[AA][EtOH] = k_{10}e^{-E_1/RT}[AA][EtOH]$  
Concentration flag: moles/volume

$r_2 = K_2[EA][H_2O] = k_{20}e^{-E_2/RT}[EA][H_2O]$  
Time Unit: Min.

$k_{10} = 29000, \quad E_1 = 7150$  
Volume Unit: Liters

$k_{20} = 7130, \quad E_2 = 7150 \quad$ Activation Energy: Cal

◎ Simulate this reactor  
Molar Flow Unit: Gm-mole

◎ This reaction is endothermic.

Change reactor type to isothermal at 100 °C. The conversion decreases. Why?
RATE DATA FOR REACTIONS
OBTAINED FROM "HOLLAND"

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<tr>
<th>Stream No</th>
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<th>FEED 2</th>
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<td>- Overall -</td>
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<td>2.0000</td>
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<tr>
<td>Temp C</td>
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<tr>
<td>Vapor mole fraction</td>
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<tr>
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<td>Ethanol</td>
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<td>Water</td>
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<td>0.1754</td>
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<tr>
<td></td>
<td>Ethyl Acetate</td>
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<td>0.1754</td>
</tr>
</tbody>
</table>

<table>
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<th>Equip. No.</th>
<th>Name</th>
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<tbody>
<tr>
<td>No. of Reactions</td>
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<tr>
<td>Specify reaction phase</td>
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<tr>
<td>Specify thermal mode:</td>
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<tr>
<td>Tout C</td>
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<tr>
<td>Vol</td>
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</table>
**Equilibrium Reactor**

\[
\ln(K_{eq}) = \ln \left( \frac{(P_1)^{x_1}(P_2)^{x_2} \cdots (P_i)^{x_i}}{(R_1)^{y_1}(R_2)^{y_2} \cdots (R_i)^{y_i}} \right) = A + \frac{B}{T}
\]

Where,

- \( P_i \) : Partial pressure or mole fraction of **product** component \( i \)
- \( R_i \) : Partial pressure or mole fraction of **reactant** component \( i \)
- \( X_i \) : Power coefficient of the **product** component \( i \)
  - generally equal to stoichiometric coefficient
- \( Y_i \) : Power coefficient of the **reactant** component \( i \)
  - generally equal to stoichiometric coefficient
- \( A,B \) : Arrhenius coefficients
- \( T \) : temperature, absolute degrees
Equilibrium Reactor

◎ Equilibrium Reactor Type
  General equilibrium reactor
  Shift reactor
  Methanation reactor

◎ Specify calculation mode
  Conversion specified
  Approach temperature. \( T = T_{\text{reactor}} + DT \)
  Approach fractional conversion \( (eq) \).
Workshop Reactor 3: Equilibrium Reactor

\[ \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightarrow \text{NH}_3 \]

- Fractional conversion of 1 mole of N\(_2\) to ammonia using excess of H\(_2\)
  - Adiabatic, \(P=200\) atm, \(T=1450\) R, \(\text{H}_2/\text{N}_2 = 3:1\) (mole ratio) in feed.

- Equilibrium data developed from figure, next page

The equation:
\[
\ln (K_{eq}) = A + \frac{B}{T}
\]

from figure
- \(K_{eq} = 0.003\) at 1452.3 R
- \(K_{eq} = 0.002\) at 1533.75 R

\(A = -13.444\)

\(B = 11088.52\)

- Simulate this reactor
Equilibrium Constant Estimation
Workshop Reactor4: Equilibrium Reactor

- Change reactor type to isothermal at 1534 R and approach fraction of 1.0. rerun (at 200 atm) and check the Keq against the attached data.

- Conclusion
  1. Keq and its correction constants (A and B) are dependent on the stoichiometric equation.
     The stoichiometric coefficients used in the data input must be consistent with those used to derive the A and B coefficients of the Keq equation.
  2. ChemCAD uses the mole fractions or partial pressures to define Keq.
     The thermodynamically correct form for Keq uses activities, which are unimportant for liquids. For gases it means that the Keq equation must be known or correlated at the reactor pressure.
**EQUILIBRIUM REACTOR**

Fractional Approach = 0.9

Equil Contents:
\[ A = -13.444, \quad B = 11088.52 \]

---

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Name</th>
<th>1</th>
<th>2</th>
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</thead>
<tbody>
<tr>
<td></td>
<td><strong>Overall</strong></td>
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</tr>
<tr>
<td>Molar flow 1bmol/h</td>
<td>4.1000</td>
<td>3.8584</td>
<td></td>
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<td>Mass flow 1b/h</td>
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<td>3.1000</td>
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<tr>
<td>Ammonia</td>
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<td>0.2416</td>
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**NH3 SYNTHESIS**
GIBBS Reactor

- Based on free energy minimization
- Similar form to equilibrium reactor
- Species derived from component list; inerts may be defined
- User components need thermo, atom data
- Approach temperature allowed
Workshop Reactor4 : GIBBS Reactor

Adiabatic equilibrium conversion of 1 mole of nitrogen to ammonia using an excess of hydrogen. Conversion is based on free energy minimization.

P=200 atm

- Simulate this reactor
- Change reactor type to isothermal at 1534 R.
  Rerun and check results against equilibrium reactor results.
- The Gibbs reactor is particularly useful where no experimental data exists on equilibrium or kinetics.
Gibbs Reactor

**Equid. No.**
Name: NH3 SYNTHESIS
Specify thermal mode: 1
R: 1646.7000
Reaction Phase: 1
Pressure atm: 200.0000

<table>
<thead>
<tr>
<th>Stream No.</th>
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<tbody>
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