Liquid & Gas Properties Module

User's Guide

COMSOL

Liquid & Gas Properties Module User's Guide

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User's Guide Introduction

This guide describes the Liquid & Gas Properties Module, an optional package that extends the COMSOL Multiphysics® modeling environment with functionality for specifying and analyzing properties of liquids and gases. The properties are tailored for transport problems such as the analysis of mass transfer, heat transfer, or fluid flow, but can be in used in any model that involves fluids.

The *Liquid & Gas Properties Module User's Guide* is a consummate guide to using the add-on module Liquid & Gas Properties Module. Instructions how to use COMSOL in general are included with the *COMSOL Multiphysics Reference Manual*. The *Introduction to the Liquid & Gas Properties Module* contains a quick-start guide to help you get started using this module.

About the Liquid & Gas Properties Module

In this section:

- The Scope of the Liquid & Gas Properties Module
- An Introduction to Using Physics Interfaces with the Liquid & Gas Properties Module
- The Liquids and Gases Material Database
- Where Do I Access the Documentation and Application Libraries?

The Scope of the Liquid & Gas Properties Module

The Liquid & Gas Properties Module provides tailor-made functionality for specifying properties of liquids and gases used in the modeling of fluid flow, energy transport, and mass transfer. The fluid properties provided are often dependent on temperature or temperature and pressure as well as on time and space. When modeling mixtures with multiple components, the impact of the chemical composition and changes therein can also be accounted for. The main components provided with module consist of a built-in properties database for chemical species, together with a thermodynamic properties calculator. When used together, these two make it possible to compute thermodynamic properties and transport properties for pure solutions and mixtures of chemical compounds in gas or liquid form. Examples of properties that can be computed are heat capacity, thermal conductivity, density, and diffusivity. The properties can furthermore often be computed using multiple models. Properties can be calculated for fluids consisting of a single gas phase or a single liquid phase and for liquid-liquid, gas-liquid, and gas-liquid-liquid systems. For multiphase systems, the equilibrium composition can also be calculated to, for example, to calculate the phase envelope for a liquid mixture at equilibrium with its gas phase (flash calculations).

All functionality provided with the Liquid & Gas Properties Module is available in the Thermodynamics node added to the Global Definitions branch of the Model Builder window. The natural way to start is to first define a Thermodynamic System including one or several compounds (chemical species) for which properties are to be defined. When the system is defined, a multitude of functions or constants describing physical properties can be created. This is accomplished using the thermodynamic features

Species Property, Mixture Property or Equilibrium Calculation. You can, for example, create a **Species Property** function describing the density of a fluid, and use this function in a fluid-flow interface. With a **Mixture Property** you can define mixture functions — that is, functions that depend on the composition of a mixture, describing, for example, density, enthalpy, or heat capacity.

For a system with constant composition, the most convenient route to fluid properties is to create a material using the Generate Material Wizard. This automates the procedure of creating a **Material** node, which in turn uses functions or parameters from a thermodynamic system. The resulting material can contain common transport properties such as density, heat capacity, heat capacity ratio, thermal conductivity and viscosity.

For users of the Reaction Engineering, or Chemistry interface, it is straightforward to couple chemical species in these with corresponding species in an existing thermodynamic system. The property parameters and functions required in the interfaces are then automatically added under the corresponding thermodynamic system.

A more complete description of the options available for calculating physical properties is available the chapter Workflow for Thermodynamics Property Calculations.

An Introduction to Using Physics Interfaces with the Liquid & Gas Properties Module

The appropriate physics interface for modeling a system can be chosen from the *Model Wizard*. The interfaces available with the Liquid & Gas Properties Module correspond to the ones available in the base package of COMSOL Multiphysics. Physics interfaces are available under the following branches: AC/DC, Acoustics, Chemical Species Transport, Fluid Flow, Heat Transfer, Structural Mechanics, and Mathematics. More interfaces and additional functionality can be introduced by obtaining other add-on modules for specific physics areas.

A common setup is in terms of mass transfer is use a Transport of Diluted Species interface together with a Laminar Flow interface to study mass transport including convection and diffusion. In this case, the density of the solvent fluid, and the diffusion coefficients of the diluted species can be defined using the functionality in the Liquid & Gas Properties Module. If the system is dependent on a varying temperature, a Heat Transfer in Fluids interface can also be included. This requires further properties,

namely the heat capacity and the thermal conductivity of the fluid. These can also be calculated using the functionality in the current module.

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In the *COMSOL Multiphysics Reference Manual:*

- Creating a New Model
- The Chemical Species Transport Interfaces
- The Fluid Flow Interface
- The Heat Transfer Interfaces

When one or several physics interfaces are chosen from the **Model Wizard** (or if you open the **Add Study** window), you select an analysis type (stationary, dynamic, or parametric) and then the modeling interfaces are available as a nodes in the **Model Builder** along with all the other nodes required for modeling (Definitions, Geometry, and so forth).

By adding another physics interface, you can account for a phenomenon not previously described in a model. To do this, right-click a **Component** node in the **Model Builder** to open the **Add Physics** window. You can do this at any stage during the modeling process. This action still retains the existing geometry, equations, boundary conditions, and current solution, which you can build upon for further development of the model.

The steps involved when using physics interfaces are detailed in the *COMSOL Multiphysics Reference Manual* (see Where Do I Access the Documentation and Application Libraries?). Some of the most important steps are:

- *Definitions* of parameters and model variables.
- Creating, importing, and manipulating a *geometry*.
- Specifying the chemical and transport *material properties*. Which naturally is what the Liquid & Gas Properties Module is design for.
- *Meshing* a modeling domain with appropriate consideration given to the reaction system's behavior.
- Solving the equations that describe a system for stationary or dynamic behavior, or as a parametric or optimization *study*.
- Analyzing *results* to present for further use.

Once a model is defined, you can go back and make changes to all the branches listed above, while maintaining consistency in the other definitions throughout. You can

restart the solver, for example, using the existing solution as an initial guess or even alter the geometry, while the equations and boundary conditions are kept consistent through the associative geometry feature. It is also useful to review the *Introduction to the Liquid & Gas Properties Module* included with the module's documentation.

In the *COMSOL Multiphysics Reference Manual:*

- Studies and Solvers
- The Physics Interfaces
- For a list of all the core physics interfaces included with a COMSOL Multiphysics license, see Physics Interface Guide.

The Liquids and Gases Material Database

A part from the properties database used by the **Thermodynamics** node, the Liquid & Gas Properties Module extends the material library with a **Liquids and Gases** material database. This contains temperature-dependent fluid dynamic and thermal properties for a number of common fluids.

- Liquids and Gases Materials Library
- Materials

Where Do I Access the Documentation and Application Libraries?

A number of online resources have more information about COMSOL, including licensing and technical information. The electronic documentation, topic-based (or context-based) help, and the Application Libraries are all accessed through the COMSOL Desktop.

If you are reading the documentation as a PDF file on your computer, the blue links do not work to open an application or content referenced in a different guide. However, if you are using the Help system in COMSOL Multiphysics, these links work to open other modules, application examples, and documentation sets.

THE DOCUMENTATION AND ONLINE HELP

The *COMSOL Multiphysics Reference Manual* describes the core physics interfaces and functionality included with the COMSOL Multiphysics license. This book also has instructions on how to use COMSOL Multiphysics and how to access the electronic Documentation and Help content.

Opening Topic-Based Help

The Help window is useful as it is connected to the features in the COMSOL Desktop. To learn more about a node in the Model Builder, or a window on the Desktop, click to highlight a node or window, then press F1 to open the Help window, which then displays information about that feature (or click a node in the Model Builder followed by the **Help** button (?). This is called *topic-based* (or *context) help*.

Opening the Documentation Window

THE APPLICATION LIBRARIES WINDOW

Each model or application includes documentation with the theoretical background and step-by-step instructions to create a model or application. The models and applications are available in COMSOL Multiphysics as MPH-files that you can open for further investigation. You can use the step-by-step instructions and the actual models as templates for your own modeling. In most models, SI units are used to describe the relevant properties, parameters, and dimensions, but other unit systems are available.

Once the Application Libraries window is opened, you can search by name or browse under a module folder name. Click to view a summary of the model or application and its properties, including options to open it or its associated PDF document.

Opening the Application Libraries Window

To open the **Application Libraries** window (|||):

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Discussion Forum	www.comsol.com/forum
Events	www.comsol.com/events
COMSOL Application Gallery	www.comsol.com/models
COMSOL Video Gallery	www.comsol.com/video
Support Knowledge Base	www.comsol.com/support/knowledgebase

2

Thermodynamics

This chapter describes how you can use the thermodynamics functionality to define thermo-physical and transport properties of liquids and gases. The properties in turn can be used when simulating any type of transport model involving mass transfer, fluid flow, or heat transfer, or when modeling chemical reaction systems.

In this chapter:

- Using Thermodynamic Properties
- Thermodynamic Models and Theory

Using Thermodynamic Properties

In this section:

Workflow for Thermodynamics Property Calculations

The thermodynamic properties database, together with the thermodynamic calculator, make it possible to evaluate physical properties of fluids such as heat capacity, thermal conductivity, density and diffusivity, as well as equilibrium compositions of two phases at equilibrium. The properties can be calculated for pure fluids, mixtures, and for two-phase fluid systems consisting of pure species as well as mixtures.

Using the thermodynamics functionality involves the following main steps:

1 Add the **Thermodynamics** node and create a thermodynamic system to add properties for a selected set of chemical compounds, referred to as chemical species in this manual. A thermodynamic system can be created in the following ways:

- A built-in **Thermodynamic System** uses the built-in, or user-defined, property database with native functionality for thermodynamic property calculations.

- An **External Thermodynamic System** uses properties from an installed external package provider. For more information on how to enable the use of external packages see the Installing External Thermodynamic Packages — An Example.

- A **Predefined System** uses the built-in database with native functionality to set up one of the following common systems; Dry air, Moist air, or Water-steam.

2 Once a thermodynamic system is set up, it can be used to define a multitude of property functions. The Generate Material option provides a fast route to defining the material properties most commonly required for fluid flow, heat transfer and mass transfer modeling. By specifying the composition and phase of the mixture, a **Material** node can automatically be set up. The material node can include properties such as density, heat capacity, heat capacity ratio, thermal conductivity and viscosity.

3 Users of the Reaction Engineering, or Chemistry interface can couple chemical species in these interfaces with the chemical species in the thermodynamic system. When Coupling with the Reaction Engineering and the Chemistry Interfaces the required property parameters and functions are automatically added and visualized as nodes under the corresponding thermodynamic system node.

4 As an alternative to the functions automatically set up when using Generate Material or coupling to, for example, Chemistry, functions or constants can be set up manually for any thermodynamic system. This is accomplished using the thermodynamic features Species Property, Mixture Property or Equilibrium Calculation. You can, for example, create a **Species Property** function describing the density of a fluid, and use this function in a fluid-flow interface. With **Mixture Property** you can define mixture functions, that is, functions that depend on the composition of a mixture, describing for example density, enthalpy, or heat capacity.

The functionalities described in Step 2– 4 generate functions and constants, defined by a thermodynamic system, that can be used in any physics interface in COMSOL Multiphysics. The functions are used to evaluate fluid properties that depend on variables such as temperature, pressure, and mixture composition. For more information, see Evaluating a Property Function in a Physics Interface.

Thermodynamics

To access the functionality for thermodynamic calculations, right-click the **Global Definitions** node in the **Model Builder** tree and select **Thermodynamics** (△). When the model includes a Component, **Thermodynamics** is also available on the **Physics** toolbar.

Using the Reaction Engineering or Chemistry interfaces, **Thermodynamics** is also available on the **Reaction Engineering** or **Chemistry** toolbar.
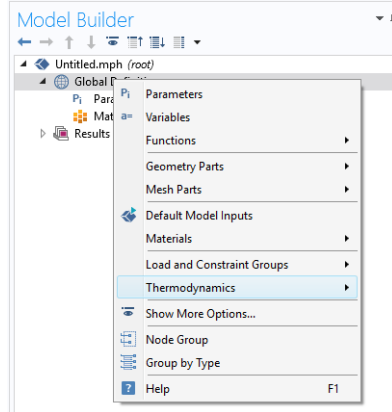
Figure 2-1: The Thermodynamics is always available under Global Definitions.

Thermodynamic properties given as parameters or functions are collected in a so called thermodynamic system. Each thermodynamic system includes a set of available species and phases, as well as different models used for the thermodynamic property calculations, for example an equation of state such as Peng–Robinson.

Select Thermodynamic System in the context menu to add a thermodynamic system that uses the built-in database included with COMSOL Multiphysics.

As an alternative, selecting External Thermodynamic System can make use of an installed thermodynamics software to make the corresponding calculations.

The option Predefined System, allows you to set up one of the following systems; Dry air, Moist air, or Water-steam.

It is also possible to import previously created and stored thermodynamic systems by selecting **Import Thermodynamic System** (see Exporting and Importing Thermodynamic Systems).

In addition to creating thermodynamic systems, you can also define User-Defined Species in Thermodynamics. Use **User-Defined Species** to add new species that are not available in the COMSOL database. You can also edit available species in the database.
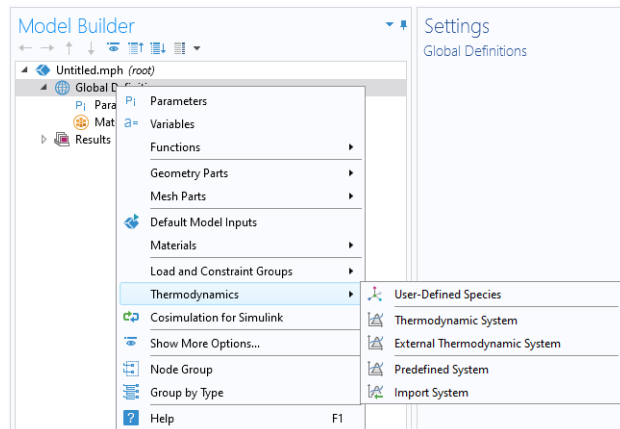
Figure 2-2: Adding Thermodynamic Systems to the Thermodynamics node. Note that external package providers have been installed.

When a thermodynamic system has been added, thermodynamic and transport properties are defined by functions. These can be used to describe properties for pure species, mixtures, and for gas-liquid (or liquid-liquid) systems at equilibrium.

Thermodynamic System

A thermodynamic system is used to describe properties of pure species and mixtures of chemical compounds for liquids, gases, liquid-vapor equilibria, and liquid-liquid equilibria. It specifies the available species and the phases (states of aggregation) that are present in the modeled system. It also defines and evaluates the functions for thermodynamic and transport properties of the chemical system, that is, the species and mixture properties for liquids, gases and phase equilibria.

To create a **Thermodynamic System**, start the **Thermodynamic System Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **Thermodynamic System**.

- Using the Reaction Engineering interface, choose **Thermodynamic System** from the **Thermodynamics** section of the **Reaction Engineering** toolbar.

- Correspondingly, using the Chemistry interface, choose **Thermodynamic System** from the **Thermodynamics** section of the **Chemistry** toolbar.

The **Thermodynamic System Wizard** contains the following steps:

1 Select System

2 Select Species

3 Select Thermodynamic Model

SELECT SYSTEM

Use the **Select System** step in the wizard to define the phases in the modeled system. You can select **Gas**, **Liquid**, **Vapor-liquid**, **Vapor-liquid-liquid**, or **Liquid-liquid**. The names of the phases in the Selected system table can be changed by editing the element in the Name column. Click the **Next** button ( ) to proceed to the next step in the wizard.

Figure 2-3: Thermodynamic System Wizard: Select System.

SELECT SPECIES

Use the **Species Type filter text** field to search among the available species in the **COMSOL** database or the User-Defined Species. Species can be searched for by typing the name, CAS number, or the chemical formula. Using a formula, all species whose chemical formula includes a combination of the given atoms are listed. For example, when searching for ammonia NH3 or H3N can be used.

Select one or more species in the list and click the **Add Selected** button ( ) to add species to the **Selected species** table. You can also press the **Enter** key to add either the

first species in the list, or the species that have been selected. To remove species from the Selected species table, use either the Remove Selected button ( ) or the Remove All button ( ), both located below the table. Click the **Next** button ( ) to proceed to the next step in the wizard.
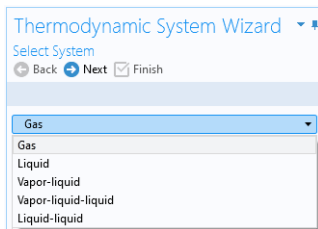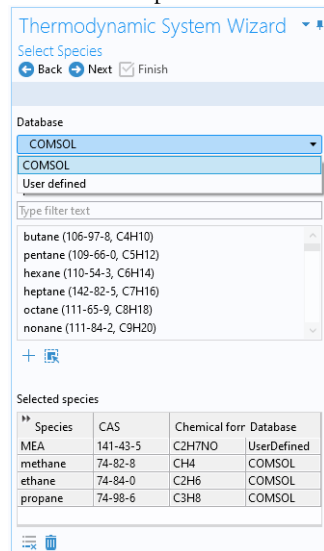

Figure 2-4: Thermodynamic System Wizard: Select Species.

SELECT THERMODYNAMIC MODEL

The Thermodynamic model controls the relations between the intensive thermodynamic properties of the system such as pressure, specific volume, and temperature. It also controls how extensive properties like enthalpy, entropy, or the heat capacity of the system are computed. Furthermore, the Thermodynamic model specifies the default models used to compute transport properties.

The following Thermodynamic Models are available for all phases:

- Peng–Robinson
- Peng–Robinson (Twu)
- Soave–Redlich–Kwong
- Soave–Redlich–Kwong (Graboski–Daubert)

For a system including only gas phase, or for liquid phase systems with thermodynamic models requiring an equation of state, the Ideal Gas Law is added to the available models in the **Gas phase model** list or **Equation of state** list.

When the system includes one or more liquid phases, the following additional models are also available (in the **Liquid phase model** list):

- Chao–Seader (Grayson–Streed)
- Wilson
- NRTL
- UNIFAC VLE
- UNIQUAC
- Regular Solution
- Extended Regular Solution
- Ideal Solution

These models correspond to activity models.

To calculate properties of water and steam, use the Water (IAPWS) model. This is available for systems that include a single water species.

For recommendations regarding the appropriate thermodynamic model, based on the available phases and the system pressure level, see the section Selecting the Right Thermodynamic Model.

Select the **Advanced options** check box in order to manually control the models used for thermodynamic properties, transport properties, and surface tension. When this check box is selected, all available property models are shown in the property model table. The available property models are dependent on the phases available in the thermodynamic system.

When only a gas phase is present, models are available for the following properties:

- Gas diffusivity
- Gas thermal conductivity
- Gas viscosity

For a single-phase liquid, or for a two-phase liquid-liquid system, there are models for the following properties:

- Liquid diffusivity
- Liquid diffusivity at infinite dilution
- Liquid thermal conductivity

- Liquid viscosity

- Liquid volume

For systems with both vapor and liquid phases, all of the above properties are available, as well as Gas-liquid surface tension.

Figure 2-5: Thermodynamic System Wizard: Advanced thermodynamic model options available for a Vapor-liquid system.

Click the **Finish** button (⊠) to exit the **Thermodynamic System Wizard** and add the corresponding system under the **Thermodynamics** node. Note that the default node label reflects the available phase in the system. For example, when creating a vapor-liquid system, a node labeled **Vapor-Liquid System** is added. The name of the system can be changed using the Label text field in the Settings window for the system.

SETTINGS

Selecting a Thermodynamic System or Predefined System node shows its **Settings** window with a description of the package content and the available properties. Editing

the text in the Label text field changes the name of the system. Below follows a description of the thermodynamic system settings.
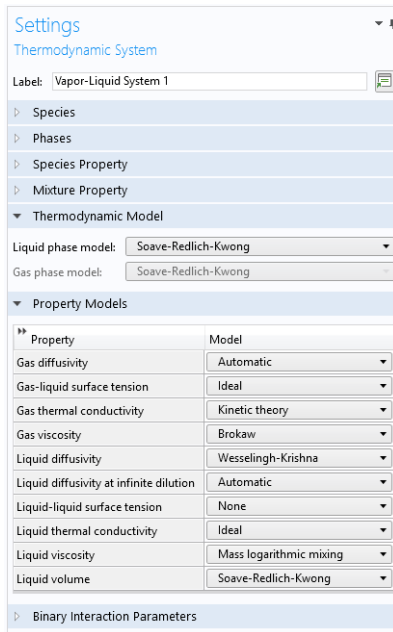
Figure 2-6: Thermodynamic System Settings.

Species:
Lists the species included in the thermodynamic system. You can change the list of species by right-clicking the **Thermodynamic System** node and selecting Add or Remove Species.

Phases:
Lists the phases included in the thermodynamic system. You can add or remove phases, such as gas, liquid or liquid-vapor, by right-clicking the **Thermodynamic System** node and selecting Define System.

Species Property:
Lists the parameters and functions that describe thermodynamics and transport properties for pure species. Such functions may describe density, heat capacity, thermal conductivity, or other thermodynamic and transport properties. For more information, see Species Property.

Mixture Property:

Lists the available mixture property functions. Note that you have to have a mixture model defined in order to use these functions. You can define a mixture property by right-clicking the **Thermodynamic System** node and selecting Mixture Property.

Thermodynamic Model:

When a liquid is present, use the **Liquid phase model** list to select the thermodynamic model for this phase.
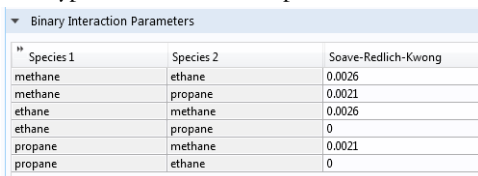
When a gas is present, use the **Gas phase model** list to select the thermodynamic model for this phase. If both gas and liquid phases are available, and the **Liquid phase model** is set to an equation of state, then the **Gas phase model** is set to the same model automatically.

Property Models:

Displays the settings for the available individual property models. The property models can be changed by selecting different values from the combo box in the Model column. For example, for **Gas thermal conductivity** you can select **Kinetic theory** or **Ideal** from the corresponding combo box. You can also select the property model in the last step of the thermodynamic system wizard by selecting the **Advanced option** check box, see Select Thermodynamic Model.

Binary Interaction Parameters:

This section can be used to inspect and edit binary interaction parameters. Select a pair of species (first and second column, Species 1 and Species 2) as shown in Figure 2-7 to edit the corresponding binary interaction parameter currently in use. In cases that the thermodynamic model has more than one type of binary interaction parameter, each type of the interaction parameter will be shown in a column in the table.

Species 1	Species 2	Soave-Redlich-Kwong
methane	ethane	0.0026
methane	propane	0.0021
ethane	methane	0.0026
ethane	propane	0
propane	methane	0.0021
propane	ethane	0

Figure 2-7: Entering the Binary Interaction Parameters for the Soave–Redlich–Kwong model.

When a binary interaction parameter is not available in the database for a pair of species, the parameter value is set to zero (default value).

It is possible to modify an existing thermodynamic system, for example by changing the included species or phases. To do so, right-click the **Thermodynamic System** node and select Add or Remove Species, or Define System from the context menu. Both of these options are available for systems created using Thermodynamic System. For a **Predefined System**, the option **Add or Remove Species** is available for Dry Air and Moist Air. For a Water-steam system, neither of the two options are available.

When the properties of a User-Defined Species have been changed, select Update From Species for the changes to take effect in the thermodynamic system.
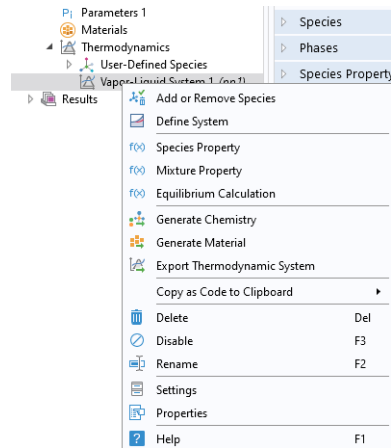
Figure 2-8: Modifying the species and phases of a thermodynamic system.

Add or Remove Species

Selecting **Add or Remove Species** takes you to the Select Species step in the **Thermodynamic System Wizard**. Use the **Add Species** button (➕) to add a species to the **Selected Species** list. To remove a species, select it in the list and use the **Remove Species** button (▤).

Make sure to click the **Finish** button (☑) in order for the changes to take effect.

Note that adding or removing species in a thermodynamic system that is currently coupled to a Reaction Engineering interface or a Chemistry interface breaks this coupling. See the Coupling with the Reaction Engineering and the Chemistry Interfaces for how to update this coupling.

Define System

Selecting **Define System** takes you to the Select System step in the **Thermodynamic System Wizard**. You can select the desired system from the list.

Make sure to click the **Finish** button (☑) button in order for the changes to take effect.

Note that changing the phase(s) in a thermodynamic system that is currently coupled to a Reaction Engineering interface or a Chemistry interface breaks this coupling. See the Coupling with the Reaction Engineering and the Chemistry Interfaces section for how this coupling can be updated.

Update From Species

This option is available in a **Thermodynamic System** that includes a User-Defined Species. Use it to update the system following a change in the species properties.

WARNING INFORMATION

A sanity check is always performed when a **Thermodynamic System** is created. If any problems are found, a Warning Information node listing the problems is added under the package. One example when this occurs is when a parameter required for the thermodynamic model, typically a binary interaction parameter, is not available in the database.

External Thermodynamic Packages

The thermodynamics functionality includes support for creating properties from external thermodynamic packages. In order to use external packages, the external software has to be CAPE-OPEN compliant. Thermodynamics in COMSOL Multiphysics supports the CAPE-OPEN Thermo 1.1 and the CAPE-OPEN Thermo 1.0 standards.

CAPE-OPEN is an open interface standard for chemical process simulation software (Ref. 1). This standard defines rules and interfaces that allows linking between compliant software. Some examples of CAPE-OPEN compliant software are:

- COCO/TEA (Free of charge package provider; see Ref. 2).
- Multiflash™ (KBC Advanced Technologies plc).
- VMGThermo™ (Virtual Materials Group, Inc.).
- Simulis® Thermodynamics (ProsSim SA).

- Aspen Properties, aspenONE® (Aspen Technology, Inc.).
- COMThermo® packages (comes with Aspen HYSYS®).

Accessing external thermodynamic systems allows species properties, mixture properties, as well as phases equilibrium calculations (gas-vapor, liquid-liquid) to be obtained from external software, such as the ones listed above.

INSTALLING EXTERNAL THERMODYNAMIC PACKAGES — AN EXAMPLE

TEA is a thermodynamics thermodynamic system that handles the physical and thermodynamic property calculations for the simulation environment COCO. The property data bank contains more than 190 commonly used chemicals, and the package exhibits more than 100 property calculation routines with their analytical or numerical derivatives. COCO is maintained by AmsterCHEM and is free to download from the Internet (Ref. 2).

To use the external physical and thermodynamic property calculations from COCO/TEA in COMSOL Multiphysics models, you need to go through the following steps:

1 Download and install COCO, which includes the TEA thermodynamic system manager. The software is available from www.cocosimulator.org/index_download.html.

2 Create and configure a thermodynamic system template that handles physical and thermodynamics calculations needed for your model. If you have already created a package template earlier, or if an adequate thermodynamic system already exists in the installation, this step is not needed.

3 Create an External Thermodynamic System node as detailed in the next section. The installed packages are available in the Select Property Package step of the Thermodynamic System Wizard.

External Thermodynamic System

The following assumes that you have installed external thermodynamic packages from a CAPE-OPEN compliant software in the manner outlined in Installing External Thermodynamic Packages — An Example.

Locate the **Thermodynamics** node and right-click to add an **External Thermodynamic System** (Figure 2-2). Using a **Reaction Engineering** or **Chemistry** interface, you can also add an external package by choosing **External Thermodynamic System** from the **Thermodynamics** section of the **Reaction Engineering,** or **Chemistry,** toolbar.

SELECT PROPERTY PACKAGE

All installed packages, from providers such as COCO/TEA, Aspen Properties, and so on, are available in the **Thermodynamic System Wizard** (Figure 2-9). Select one of the packages and click the **Finish** button ( ) in the upper right corner of the wizard in order to add the package as an **External Thermodynamic System** node under the **Thermodynamics** node.

When adding the package its default label reflects the included phases. For example, a node labeled **Vapor-Liquid System (External)** is created when adding an external package containing a vapor and a liquid phase. The name of the system can be changed using the Label text field in the Settings window for the system.
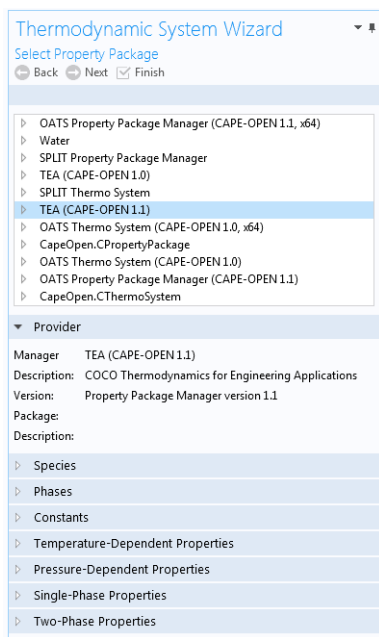
Figure 2-9: Available external thermodynamic systems. Use the Thermodynamic System Wizard to browse the contents of the installed external thermodynamic systems on your system. The example shows the packages shipped with the COCO provider.

SETTINGS

Selecting the **External Thermodynamic System** node shows the thermodynamic system settings with sections for available species, phases, species properties, and mixture properties. Editing the text in the Label text field changes the name of the system. Below follows a description of the thermodynamic system settings.

Provider
Contains information about the external thermodynamic system provider such as version, CAPE-OPEN compliance, and a short description of the external software that provides the thermodynamic system.

Species
Lists the species included in the selected thermodynamic system.

Phases
Lists the phases included in the selected thermodynamic system for example gas, liquid, gas-vapor, or liquid-liquid.

Species Properties
Lists the parameter values or the functions that describe species properties, for example molar mass, and properties available for pure compounds, such as density as a function of temperature.

Mixture Properties

Lists the available functions that describe mixture properties. One example is the density of a nonideal mixture as a function of composition.
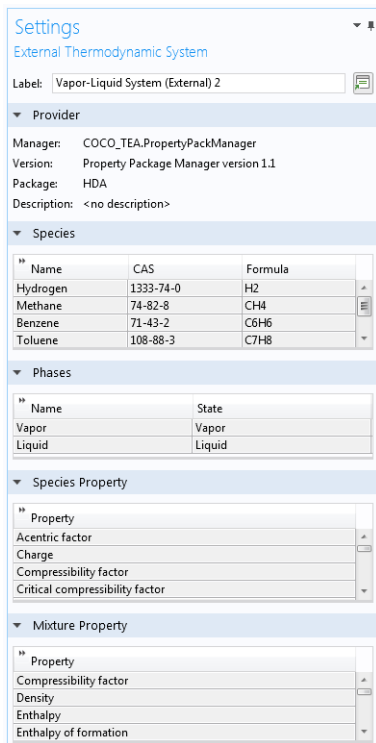
Figure 2-10: Settings window for an External Thermodynamic System.

The thermodynamic functionality supports package *persistence*. This means that an mph-file for a model that uses a thermodynamic system stores that package definition in the file. You can use the mph-file to access a thermodynamic system defined in the corresponding model without having to store the thermodynamic system as a separate file.

Predefined System

A **Predefined System** uses the built-in database with native functionality to set up one of the following common systems; dry air, moist air, or water and steam.

To create a **Predefined System**, start the **Thermodynamic System Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **Predefined System**.

- Using the Reaction Engineering interface, choose **Predefined System** from the **Thermodynamics** section of the **Reaction Engineering** toolbar.

- Correspondingly, using the Chemistry interface, choose **Predefined System** from the **Thermodynamics** section of the **Chemistry** toolbar.

The **Thermodynamic System Wizard** that opens is identical to the wizard used to create a Thermodynamic System, but with the important difference that all settings have been entered for the chosen predefined system. The wizard contains the following steps:

1 Select System

2 Select Species

3 Select Thermodynamic Model

SELECT SYSTEM

In the Select System window, choose one of the predefined systems in the list. Choose among **Dry air**, **Moist air** and **Water-steam**. Click the Next button (➡) to proceed to the next step in the wizard.
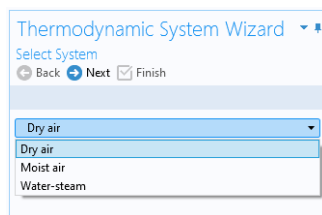
Figure 2-11: Thermodynamic System Wizard: Select Predefined System.

SELECT SPECIES

If Dry or Moist air was chosen in the Select System step, the **Selected species** table is populated with the species relevant for the chosen system. For Dry air the species are: nitrogen, oxygen, argon, carbon dioxide, neon and helium. For Moist air the list also contains water. If instead Water-steam was chosen in the Select System step, the Next button in that step guides you directly to the Select Thermodynamic Model pane. No additions of species can be done in the wizard.

To add more species to the Dry air and Moist air systems, use the **Species Type filter text** field to search among the available species in the **COMSOL** database or the User-Defined Species. Species can be searched for by typing the name, CAS number, or the chemical formula. Select one or more species in the list and click the **Add Selected** button (—) to add species to the **Selected species** table. To remove species from the Selected species table, use either the Remove Selected button ( ) or the Remove All button ( ), both located below the table. Click the **Next** button ( ) to proceed to the next step in the wizard.
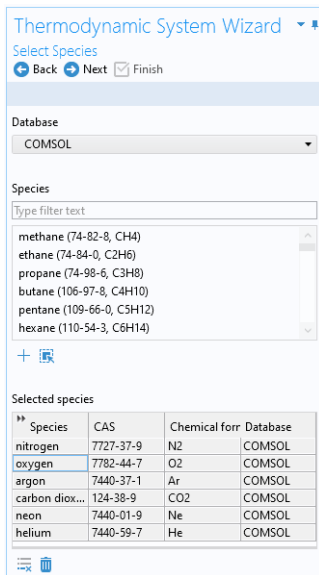
Figure 2-12: Thermodynamic System Wizard: Select Species.

SELECT THERMODYNAMIC MODEL

This last step of the Thermodynamic System Wizard allows you to choose what thermodynamic model to use. For the system Dry air and Moist air, the Ideal Gas law is chosen by default. For Water-steam, the model Water (IAPWS) is used. For more information about this step in the Thermodynamic System Wizard, see Select Thermodynamic Model for Thermodynamic System.

Click the **Finish** button ( ) to exit the **Thermodynamic System Wizard** and add the corresponding **Predefined System** under the **Thermodynamics** node. Note that the default node label reflects the chosen predefined system.

SETTINGS

Selecting a **Predefined System** node shows its **Settings** window with a description of the package content and the available properties. For information about the content in the Settings window, see Settings for **Thermodynamic System** and **Predefined System**.

MODIFYING A PREDEFINED SYSTEM

Please see Modifying an Existing System for information about how to modify an existing thermodynamic system.

Exporting and Importing Thermodynamic Systems

EXPORT THERMODYNAMIC SYSTEM

Right-click the thermodynamic system node for the thermodynamic system that you want to export (Figure 2-8) and select **Export Thermodynamic System**. Use the **Select File** window to store the thermodynamic system.

Note that only the thermodynamic system definition is exported, for example the underlying species data (from the database), the included phases, and the applied thermodynamic models. Property values and functions created using the thermodynamic system are not stored.

IMPORT THERMODYNAMIC SYSTEM

Right-click the **Thermodynamics** node and select **Import Thermodynamic System** (Figure 2-2). Use the **Select File** window to navigate to a thermodynamic system file and click **Open**.

It is possible to manually modify the species properties, such as parameters and temperature-dependent functions, in the created Thermodynamic System by using **Export Thermodynamic System** and **Import Thermodynamic System**. In the saved xml file from **Export thermodynamic system**, there are all parameters and temperature-dependent properties for species, which are saved inside a <Compound CompID="name"></Compound> block. For example, to edit the acentric factor of methane from 0.01141 to 0.2 perform the following steps

• Open the saved xml file for the thermodynamic system

• Find the compound methane which starts with the line:

  <Compound CompID="methane">
• Find the line with the acentric factor and change it to

  <AcentricFactor >0.2</AcentricFactor>.

To use the system with the updated species, right-click the Thermodynamics node and select Import System.

For temperature-dependent functions, for example for the (saturated) liquid density, the database input is of the form:

```
<Density>
   <Phase>Liquid</Phase>
   <Coefficients>Tlb;a0;a1;a2;a3;Tub</Coefficients>
   <Data>Tlb;f(Tlb);Tub;f(Tub)</Data>
<Comment></Comment>
</Density>
```

Here T_{lb} and T_{ub} defines the lower and upper bound for a temperature range, and a_1 to a_4 are the corresponding coefficients for a cubic polynomial as $f(T) = a_0 + a_1T + a_2T^2 + a_3T^3$ fitted for that range. Multiple sequential ranges can be added by appending temperature ranges and coefficient sets. The `<Data></Data>` block can be used to input data points directly.

The unit for temperature is K. The unit used for the temperature dependent properties (fitted polynomials functions) are defined in the table below:

TABLE 2-1: UNIT FOR TEMPERATURE-DEPENDENT PROPERTIES.

PROPERTY	UNIT
Liquid density	mol/m^3
Ideal heat capacity	J/mol/K
Ln vapor pressure	1
Heat of vaporization	J/mol
Vapor viscosity	Pa·s
Ln liquid viscosity	1
Vapor thermal conductivity	W/m/K
Liquid thermal conductivity	W/m/K
Surface tension	N/m

Species Property

A **Species Property** is used to define and compute a pure species property. The available properties consist of both parameters and functions. Some examples of available parameters are molar mass, Lennard Jones diameter, and dipole moment. Some examples of available functions are density, enthalpy, heat capacity, and viscosity. The property functions created are either dependent on temperature alone, or both on

temperature and pressure. For all property functions, the first order derivative with respect to temperature and, when applicable, with respect to pressure are automatically defined. The second-order derivatives with respect to temperature and pressure are available for property functions of density and molar volume.

Right-click the relevant **Thermodynamic System** node (see Figure 2-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Species Property** (f(x)) to start the **Species Property Wizard**.

The **Species Property Wizard** contains the following steps:

1 Select Properties

2 Select Phase

3 Select Species

4 Species Property Overview

SELECT PROPERTIES

First use the **Amount base unit** list to define the base unit. Select **mol** or **kg**.

Use the filter to search among the available properties. Select one or more properties in the list and click the **Add Selected** button (+) to add them to the **Selected properties** list.

Click the **Next** button () to proceed to the next step, selecting the phase.
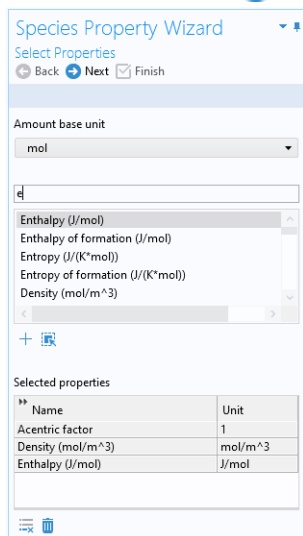
Figure 2-13: Species Property Wizard; Select Properties.

SELECT PHASE

Use the list to specify the phase for the species property. The available phases correspond to the ones defined for the thermodynamic system.
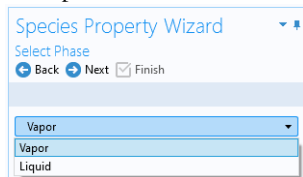
Figure 2-14: Species Property Wizard; Select Phase.

Note that for parameters (constants) this step is skipped.

Click the **Next** button () to proceed to the next step, selecting the species.

SELECT SPECIES

Select one or more of the species available in the thermodynamic system and use the **Add Selected** button () to add them to the **Selected species** table. One property function is created for each of the selected species.

Click the **Next** button ( ) to proceed to the Species Property Overview in the wizard.
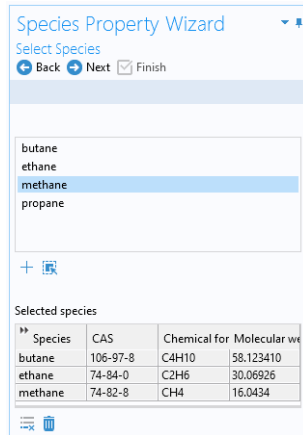
Figure 2-15: Species Property Wizard; the Select Species step.

SPECIES PROPERTY OVERVIEW

The final step of the wizard presents an overview of the parameters and functions defined for the corresponding property. Click the **Finish** button ( ) to exit the wizard and add the species property to the current thermodynamic system.

THE SPECIES NODE UNDER A SYSTEM

When creating a species properties, the resulting parameters and functions are collected under a node with the species name. You can create new functions from an existing species node under the system. Right-click the species and select **Species Property** to start the **Species Property Wizard**.
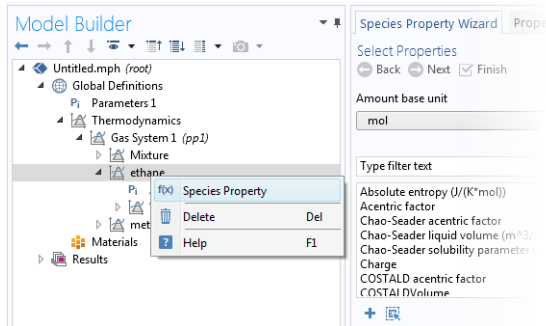
Figure 2-16: Create a Species Property from an existing species node.

Selecting a **Species Property** node shows the settings for such property.
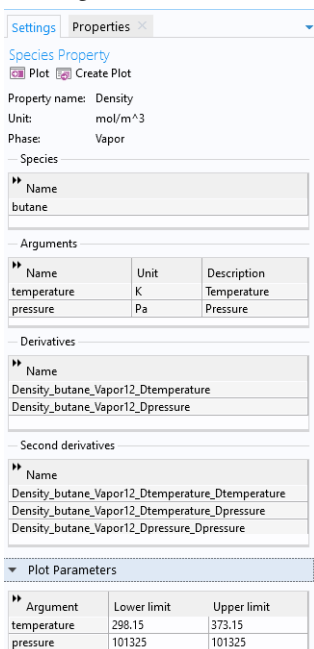
Figure 2-17: Species Property settings.

Definition:

Shows the definition of a property that is defined as a parameter or a function, for example the name of the parameter or function.

You can use the **Parameter name** or **Function name** fields to specify or change the name of a parameter or a function. The section also provides information about the property type and the species it is defined for.

For a parameter, this section also displays the numerical value.

For a function, this sections displays the arguments for the functions and the first order derivatives with respect to these arguments.

Plot Parameters

Available for property functions in order to plot a selected function for a given set of argument values.

Apply a **Lower limit** and an **Upper limit** for each argument, and click the **Plot** button (▢) to plot the function using the given argument range. You can also click the **Create Plot** button (▢) in order to create a plot group, under the **Results** node.

Properties Window

To see the reference for constant or temperature dependent functions, right-click on the function and select **Properties**. This opens the Properties window.
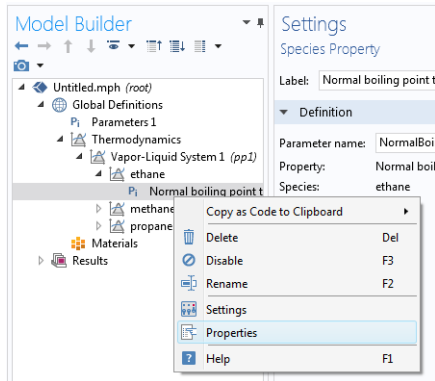
Figure 2-18: Show constant and temperature dependent properties references for species functions.

The reference for the constant or temperature dependent property is available in the **Comments** field in the **Node Properties** section.
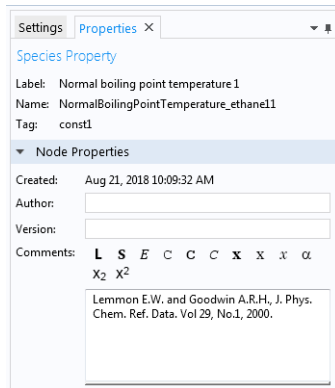
Figure 2-19: Properties window for species function.

Mixture Property

A **Mixture Property** is used to compute a property function that depends on the concentration of the species in a thermodynamic system. Some examples of the available property functions are density, enthalpy, heat capacity, and surface tension.

Apart from the composition, the mixture property functions are also dependent on temperature and pressure. The first-order derivatives with respect to temperature and pressure are automatically defined. The second-order derivatives with respect to temperature and pressure are available for property functions of density and molar volume.

Right-click the relevant **Thermodynamic System** node (see Figure 2-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Mixture Property** to start the **Mixture Property Wizard**.

The **Mixture Property Wizard** contains the following steps:

1 Select Properties

2 Select Phase

3 Select Species

4 Mixture Property Overview

SELECT PROPERTIES

The settings in this step corresponds to those for Select Properties in the **Species Property Wizard**. Click the **Next** button (➡) to proceed to the next step.

SELECT PHASE

Use this list to specify the phase, among the ones available in the system, for the selected mixture property.

Some properties require that the system consists of two phases, for example surface tension. A two-phase system may consist of a combination of liquid-vapor or liquid-liquid phases.

SELECT SPECIES

First select the **Species composition** base unit to be used for function arguments. Select **Mole fraction** or **Mass fraction**.

Select the species to be included in the list. Use the **Add All** button (🔳) to add all species in the thermodynamic system. It is also possible to select a subset of the

available species. In that case use the **Add Selected** button (+) to add species. The **Selected species** table is updated as you add species.

Click the **Next** button (→) to proceed to the next step in the wizard.

MIXTURE PROPERTY OVERVIEW

The final step of the wizard displays an overview of the functions that the wizard has added. Click the **Finish** button (☑) to exit the wizard and add the properties to the current thermodynamic system.

SETTINGS

Selecting a desired **Mixture Property** node to display its settings window.

THE MIXTURE NODE UNDER A SYSTEM

When creating mixture properties, the resulting functions are collected under the **Mixture** node. You can create new functions from an existing **Mixture** node. Right-click the node and select **Mixture Property** from the context menu to start the **Mixture Property Wizard**.
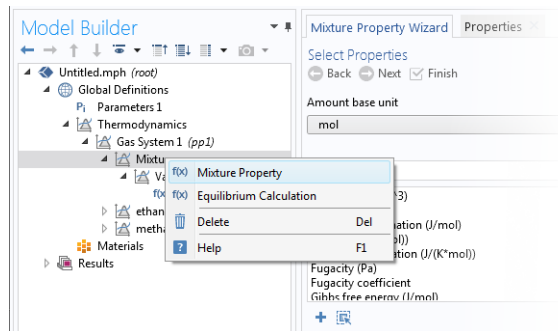
Figure 2-20: Mixture properties can be created by right-clicking a Mixture node under a thermodynamic system.

Equilibrium Calculation

The **Equilibrium Calculation** functionality is used to compute the resulting equilibrium conditions for a mixture of a set of species and phases.

Equilibrium calculations are often used for processes with vapor-liquid equilibrium (VLE), so-called flash calculations. A typical process that requires flash calculations is a distillation process, where a multiphase feed stream is separated into a vapor and a liquid product, and where the concentrations of the species in each phase are required.

Equilibrium calculations involve combining the VLE-equations with material balances for the chemical species, and in some cases with an energy balance. Flash calculations are typically used to obtain estimates of:

• Bubble point at given temperature.

• Bubble point at given pressure.

• Dew point at given temperature.

• Dew point at given pressure.

• Equilibrium conditions at given pressure and temperature.

• Equilibrium conditions at given pressure and enthalpy.

• Equilibrium conditions at given pressure and entropy.

• Equilibrium conditions at given internal energy and specific volume.

The last three examples are often considered more difficult, since they require energy balances and relations for computing enthalpy and entropy. Thermodynamics in COMSOL Multiphysics can handle all of the above cases using the equilibrium calculation functionality. Phase envelopes, bubble point, and dew point can be calculated for any number of species.

Right-click the relevant **Thermodynamic System** node (see Figure 2-8), **Predefined System** node, or the relevant **External Thermodynamic System** node, and select **Equilibrium Calculation** to start the **Equilibrium Calculation Wizard**.

The **Equilibrium Calculation Wizard** consists of the following steps:

1 Select species

2 Equilibrium Specifications

3 Equilibrium Function Overview

The **Equilibrium Calculation** settings include three types of equilibrium functions.

• The first function type is used to detect whether a phase is present in the system and includes "exist" in its name.

• The amount function computes the total amount of material in each phase.

• The phase composition functions compute the mass or mole fraction of each species in each phase, depending on the selected base unit for the equilibrium calculation.

Select one or more of the species available in the thermodynamic system and use the **Add Selected** button (➕) to add them to the **Selected species** table. Click the **Next** button (🔵➡) to proceed to the next step in the wizard.

EQUILIBRIUM SPECIFICATIONS

Use the **Amount base unit** list to use either **kg** or **mol** as base unit.

Select two **Equilibrium conditions** that define the current equilibrium, for example a given pressure and a temperature. These equilibrium conditions are used as arguments in the equilibrium functions, in addition to the composition (overall fractions of species).

The available equilibrium conditions are: **Temperature**, **Pressure**, **Phase fraction**, **Energy** (or **Internal energy of formation**), **Enthalpy** (or **Enthalpy of formation**), **Specific volume**, **Density** and **Entropy** (or **Entropy of formation**). For chemical reactions, it is recommended to use **Enthalpy of formation**, **Entropy of formation,** or **Internal energy of formation**, since they account for heat of reactions.
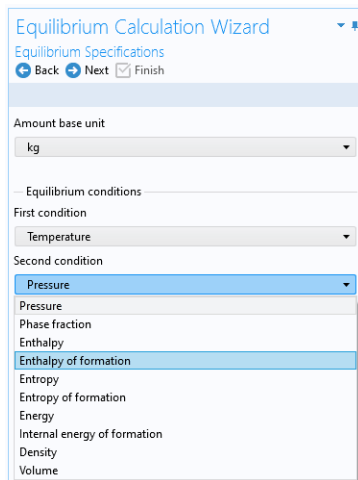
Figure 2-21: Equilibrium Calculation Wizard; Equilibrium Specifications.

Selecting **Phase fraction** as one of the equilibrium conditions activates the **Solution type** input field. This can be used to indicate the direction of the desired solution, which is of great use especially near critical points. The options **Undefined**, **Normal**, or **Retrograde** define different directions for the search of the solution to the equilibrium equations. Using **Normal** means that the derivative of the vapor phase fraction with respect to

temperature (at constant pressure and composition) is kept positive and the derivative of the vapor phase fraction with respect to pressure (at constant temperature and composition) is kept negative. Using **Retrograde** means that the opposite sign of the previous mentioned derivatives are enforced.

For a single species, the critical point is the highest pressure and temperature at which two phases (liquid and vapor) are distinguishable. However, for some multispecies systems, the critical point is a point between the dew point and the bubble point. In this case, the critical point does not represent the maximum pressure or the maximum temperature of vapor-liquid coexistence. This phenomenon is known as retrograde condensation. This means that under isothermal conditions, when the pressure decreases, some of the vapor condenses into liquid instead of expanding or vaporizing. An example of such system is formation of liquid hydrocarbons in a gas reservoir as the pressure decreases below the dew point pressure. In this case, setting **Solution type** to **Normal** or **Retrograde** may not be sufficient to distinguish between the two solutions.

Note that the **Solution type** setting is only available for a built-in thermodynamic systems. For external thermodynamic systems, the corresponding functionality needs to be supplied by the thermodynamic software provider. For instance, the COCO/TEA provider does not support the **Normal** or **Retrograde** options. In those cases, the **Solution type** should be **Undefined**.

Click the **Next** button ( ) to proceed to the next step.

EQUILIBRIUM FUNCTION OVERVIEW

In this step, you can review all the functions including units and arguments. Click the **Finish** button (⌧) to exit the wizard and add functions at equilibrium state to the current thermodynamic system.

THE EQUILIBRIUM CALCULATION NODE

When creating an **Equilibrium Calculation**, the resulting functions are collected under the **Mixture** node. You can create new functions from an existing **Mixture** node. Right-click it and select **Equilibrium Calculation** to start the **Equilibrium Calculation Wizard** (see Figure 2-20).

SETTINGS

Selecting an **Equilibrium Calculation** node displays the settings including the property functions, see Figure 2-22.

Plot Parameters:

Can be used to evaluate and plot the equilibrium function for a range of argument values. First specify which of the included functions to plot. Then apply a **Lower limit** and **Upper limit** for each argument and click the **Plot** button (⊡).
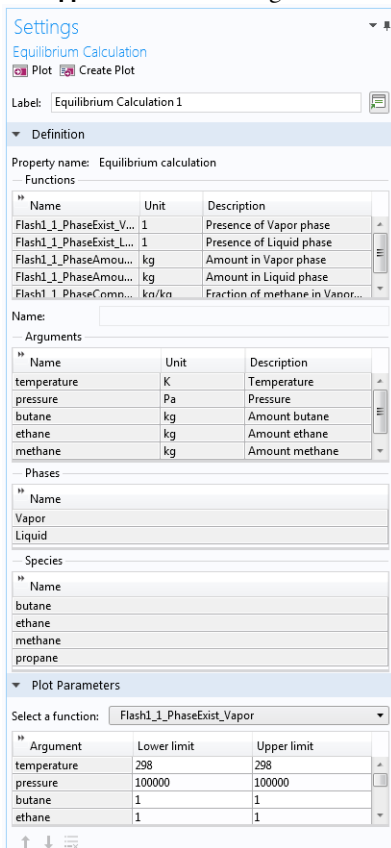
Figure 2-22: Settings window; Equilibrium calculation.

Generate Chemistry

The Chemistry physics interface includes functionality to automatically define and use mixture properties by interfacing to a Thermodynamic System node. How to manually set this coupling up is described in Coupling with the Reaction Engineering and the Chemistry Interfaces.

The **Generate Chemistry Wizard** can be used to directly create a Chemistry physics interface from an existing Thermodynamics System node. The resulting Chemistry interface is automatically populated with the selected species, and is set up to be fully coupled to the thermodynamics. This means for example that functions for mixture properties, like the density enthalpy, are automatically defined and used in the generated Chemistry interface.

Right-click the relevant **Thermodynamic System** node, **Predefined System** node, or **External Thermodynamic System** node, and select **Generate Chemistry** to start the **Generate Chemistry Wizard**.

The **Generate Chemistry Wizard** contains the following steps:

1 Select Species
2 Chemistry Settings

SELECT SPECIES

Select the species to be included in the list. Use the **Add All** button (🔲) to add all species in the thermodynamic system. It is also possible to select a subset of the available species. In that case use the **Add Selected** button (➕) to add species. The **Selected species** table is updated as you add species.

Click the **Next** button (➡) to proceed to the next step in the wizard.

CHEMISTRY SETTINGS

The table at the top shows the selected species and their respective chemical formula. For each species, a corresponding Species feature will be added in the Chemistry interface. As an option, use the **Name in Chemistry** columns to specify another name of the species in Chemistry. This means that the species name could be different in Thermodynamics and Chemistry for a species. By default the chemical formula is used.

Component

Use the **Component** list to select the model component to which the Chemistry interface will be added. The already existing components are shown in the top of the list. A new component can be created by selecting the desired space dimension.

Mass Transfer

The **Mass transfer** list controls the intended mixture type for the Chemistry interface. Select **Diluted species** to model a mixture where the species are assumed diluted in a high concentration solvent. For this choice, also select **Solvent**. Optionally, select **Concentrated species** to model a mixture where all species are assumed to contribute to

the mixture properties. In the resulting Chemistry interface the **Type** setting in the Mixture Properties section is defined accordingly.

Phase
Select the Phase of the mixture from the **Phase** list. Included in the list are the phases available in the Thermodynamic System from which the Chemistry is generated.

Click the **Finish** button (☑) to create the desired Chemistry physics interface and exit the wizard.

Generate Material

Once a thermodynamic system is defined, it can be used to define a multitude of property functions. The Generate Material option provides a fast route to defining the material properties most commonly required for fluid flow, heat transfer and mass transfer. By specifying the composition and the phase of the mixture, a Material node can automatically be setup. The material node can include properties such as the density, heat capacity, heat capacity ratio, thermal conductivity, viscosity and the diffusivity. Two types of property functions can be used, either functions from the underlying thermodynamics or interpolation functions created from these. For space-dependent models, the interpolation models are more computationally efficient.

Right-click the relevant **Thermodynamic System** node (or an **External Thermodynamic System** node or **Predefined System** node), and select **Generate Material** to start the **Generate Material Wizard**.

The **Generate Material Wizard** contains the following steps:

1 Select Phase

2 Select Species

3 Select Properties

4 Define Material

SELECT PHASE
Use this list to specify the phase of the material. Select among the ones available in the system. This step of the Generate Material Wizard is not available for the **Predefined Systems Dry Air** and **Moist Air**.

Click the **Next** button (➡) to proceed to the next step in the wizard.

SELECT SPECIES

Select the species to be included in the list. Use the **Add All** button (▣) to add all species in the thermodynamic system. It is also possible to select a subset of the available species. In that case use the **Add Selected** button (+) to add species. The **Selected species** table is updated as you add species.

Notice that when using Generate Material for the **Predefined System Water-steam** this step is not included in the wizard.

Material Composition

Specify the mixture composition in terms of the **Mole fractions** or **Mass fractions** of all species. The fractions should sum to one. This setting is only available for systems with more than one component, and for materials with more than one selected species.

Click the **Next** button (➡) to proceed to the next step in the wizard.

SELECT PROPERTIES

Use this step to select the material properties to be included.

For a liquid phase material the following properties are available:

- Density, (ρ)
- Diffusion coefficient at infinite dilution
- Heat capacity (C_p)
- Thermal conductivity (k)
- Viscosity (μ)

For a gas phase material, the Heat capacity ratio ($\gamma = C_p/C_v$) is also available.

To add a property to the **Selected properties** list click the **Add Selected** button (+). To remove properties, use the **Remove Selected** button (▤) or the **Remove All** button (🗑)

When adding the **Diffusion coefficient at infinite dilution**, also select which of the species is the solvent. The material will include one diffusion coefficient for each of the remaining (solute) species.
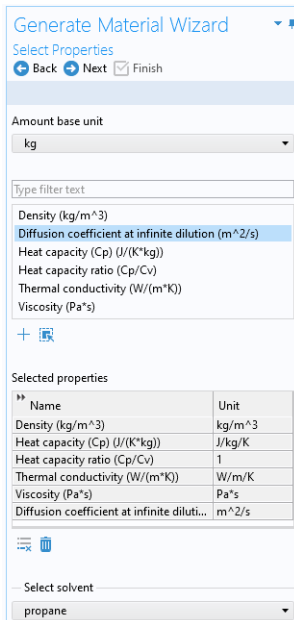
Figure 2-23: Generate Material Wizard; Select Properties with Diffusion coefficient at infinite dilution added.

Additional properties

The below additional properties are defined from the selected properties and added to the output properties of the material.

For a liquid phase material the isobaric coefficient of thermal expansion is defined as

$$\alpha_{iso} = -\frac{1}{\rho}\frac{\partial\rho}{\partial T} \tag{2-1}$$

For a gas phase material, the speed of sound c, and the isentropic compressibility χ_f are also defined as

$$c = \sqrt{\gamma\frac{\partial p}{\partial\rho}}, \qquad \chi_f = \frac{1}{\gamma\rho}\frac{\partial\rho}{\partial p} \tag{2-2}$$

Click the **Next** button ( ) to proceed to the next step.

Component

Use the **Component** list to select where the Material will be added. The already existing components are shown in the top of the list. A new component can be created by selecting the desired space dimension. Select **Global** at the end of the list to add the material under **Global Definitions**. A global material can be utilized in any component, through the use of a Material Link. It can also be used to define phase specific properties when linked to a subnode of a **Porous Material**.

Function Type

The material can be set up to use functions defined under the thermodynamics system, or interpolation functions defined from these. The interpolation functions are significantly faster to evaluate, especially for space dependent models, but requires that the temperature range and the pressure range are specified.

Select **Thermodynamics** to base the material properties on functions in the current thermodynamic system. The required functions are created, if not already present, and added to the system. When evaluating material properties, the underlying thermodynamics functions are called.

Select **Interpolation** to generate interpolation functions for the material properties. In this case the required functions are first created and added to the system. Next, the functions are evaluated in a number of sampling points over a given range, for both temperature and pressure. The result of the evaluation is stored and used to define interpolation functions for all material properties.

For the **Interpolation points**, select **Same for all functions** to use the same number of evaluation points for all functions. By selecting **Individual**, the number of evaluation points can be given per function. The latter can for example be used to increase the number of points for a function that is known to vary faster than the rest of the functions.

Select one of the preset levels for the **Maximum number of interpolation points**. This is used to provide a maximum size of the underlying data for the interpolation functions. If the total number of evaluation points for any function, varying temperature and pressure, is exceeded, a warning is shown.

Define the temperature range and pressure ranges for the temperature and pressure by providing the **Low** and **High** end values. To neglect the variation in either temperature or pressure, give the same value for the low and high end value. This can for example be used when the pressure variation is known to be negligible. For each range, also

define the number of evaluation points in the **Number of points** field. The underlying functions are evaluated at uniformly distributed positions across the temperature and pressure range.

When **Individual** has been selected for the **Interpolation points**, the **Ranges and interpolation points** can be specified per function to be created.

Click the **Finish** button (☑) to create the specified Material and exit the wizard.

Coupling with the Reaction Engineering and the Chemistry Interfaces

Using the **Reaction Engineering** or **Chemistry** interfaces, all species property parameters and property functions required by these interfaces can be created automatically by coupling to an existing **Thermodynamic System**, **Predefined System**, or **External Thermodynamic System** under **Thermodynamics**. Examples of species properties that can be created automatically are molar mass, heat capacity, enthalpy, and entropy for each species. Parameters and functions for these properties are created by the thermodynamic system. The **Reaction Engineering** and **Chemistry** interfaces can also be used to define transport properties for the resulting mixture (all species in the interface). When coupled, the following mixture properties can be automatically created: heat capacity, density, thermal conductivity, and dynamic viscosity.

> ⚠ The Reaction Engineering interface and the Chemistry interface are only available in a limited set of add-on products. See https://www.comsol.com/products/specifications/ for more details on availability.

Note that using a thermodynamic system significantly increases the modeling capabilities in the **Reaction Engineering** and **Chemistry** interfaces. All ideal and nonideal thermodynamic models, for gases and liquids, are directly available and also automatically updated by editing the settings for the thermodynamic system in use. The **Chemistry** interface can furthermore be used to make the mixture properties readily available in space-dependent models for modeling of mass transport, heat transfer, or fluid flow.

REACTION ENGINEERING

Mixture Properties

You can couple a Reaction Engineering interface with an existing thermodynamic system in the **Reaction Engineering** interface's settings window.

You need to have at least one species defined in the Reaction Engineering interface in order to couple it to a thermodynamic system. You can make this coupling in the Settings window for the **Reaction Engineering** interface by selecting the **Thermodynamics** check box in the **Mixture Properties** section.

Select a thermodynamic system from the **Thermodynamic system** list. Use the **Phase** list to select the phase to be used in the **Reaction Engineering** interface.
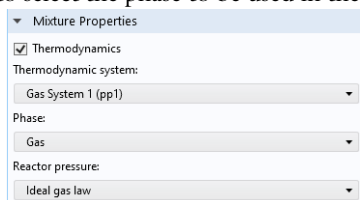
Figure 2-24: Coupling Reaction Engineering Interface with Thermodynamics.

Species Matching

The **Species Matching** section is activated when the **Thermodynamics** check box is selected in the **Mixture Properties** section; see above. The species in the Reaction Engineering interface can be matched to a species in the thermodynamic system. This step ensures that the arguments in the thermodynamic system functions are correctly defined.

Use the lists in the **From Thermodynamics** column to match each species in the interface to a species in the coupled thermodynamic system.

For each species matched, the required property parameters and functions are added under to the corresponding thermodynamic system.

When all species are matched, the interface is considered fully coupled and functions representing mixture properties, such as density, are also added automatically under the corresponding thermodynamic system.
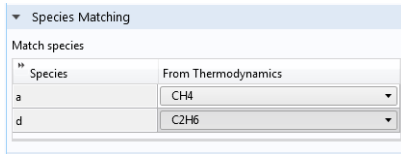
Figure 2-25: Matching the species in Reaction Engineering to those in the corresponding thermodynamic system.

Calculate Transport Properties

When the interface is fully coupled to a thermodynamic system, property functions for the mixture transport properties are created automatically when the **Calculate mixture properties** check box is selected. The properties calculated by the thermodynamic system display **Thermodynamics** in the corresponding list; see below.
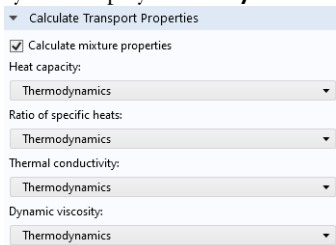
Figure 2-26: Select the Calculate mixture properties check box when coupled to a thermodynamic system.

CHEMISTRY

Mixture Properties

You can couple a Chemistry interface with an existing thermodynamic system in the **Chemistry** interface's settings window. You can make this coupling in the Settings window for the **Chemistry** interface by selecting the **Thermodynamics** check box in the **Mixture Properties** section. You need to have at least one species defined in the Chemistry interface in order to couple it to a thermodynamic system.

Select a thermodynamic system from the **Thermodynamic system** list. Use the **Phase** list to select the phase to be used in the **Chemistry** interface.

Species Matching

The **Species Matching** section is activated when the **Thermodynamics** check box is selected in the **Mixture Properties** section. Here you can match the variables for the concentrations, and by this calculate mixture properties (transport and thermodynamic properties). For information on how to specify the dependent variables to be used, see Species Matching in The Chemistry Interface documentation in the *Chemical Reaction Engineering Module User's Guide*.

You can match the species in the Chemistry interface with those in the corresponding thermodynamic system in the **Species matching** section's table. Use the lists in the column with the title **From Thermodynamics** to match each species in the Chemistry interface to a species in the corresponding thermodynamic system. This ensures that the composition function arguments in the thermodynamic system are correctly defined.

For each species matched, the species property parameters and functions required by the Chemistry interface are automatically created and added under the corresponding thermodynamic system.

When all species are matched, the interface is fully coupled to Thermodynamics and functions representing mixture properties, such as the density, are added automatically under the thermodynamic system that the interface is coupled to.

Figure 2-27: Matching concentration variables in a Chemistry interface, as well as species in a coupled Thermodynamic System.

Calculate Transport Properties

When the interface is fully coupled to a thermodynamic system, property functions for the mixture transport properties are created automatically when the **Calculate mixture properties** check box is selected. The properties calculated by the thermodynamic system display **Thermodynamics** in the corresponding list; see Figure 2-26.

MIXTURE PROPERTY DEFINITIONS WHEN COUPLING TO THERMODYNAMICS

When all species in a physics interface (**Reaction Engineering** or **Chemistry**) are matched to the corresponding species in a thermodynamic system, the mixture properties are calculated based on the composition of the mixture. For example, consider $Z_{\mathrm{mix}}(T, P, n_1, ..., n_m)$, which denotes a generic extensive mixture property for a mixture of m number of species. The property function's arguments are the temperature T, the pressure P, and the number of moles, n, for each species.

When the system is fully matched, the mixture property Z_{mix} is defined as

$$Z_{\mathrm{mix}} = \sum_{i=1}^{m} n_i \bar{Z}_i \tag{2-3}$$

where $\bar{Z}_i$ is the partial molar of species i:

$$\bar{Z}_i = \left(\frac{\partial Z_{\mathrm{mix}}(T, P, n_1, n_2, ..., n_m)}{\partial n_i} \right)_{T, P, n_{j \neq i}} \tag{2-4}$$

The definition of partial molar properties can be rewritten using mole fraction derivatives as:

$$\bar{Z}_i(T, P, n_1, ..., n_m) = \bar{Z}_i(T, P, x_1, ..., x_m) = \tag{2-5}$$

$$\left(Z_{\mathrm{mix}}(T, P, x_1, ..., x_m) + \left(\frac{\partial Z_{\mathrm{mix}}(T, P, x_1, ..., x_m)}{\partial x_i} \right)_{T, P, x_{i \neq j}} \right.$$

$$\left. - \sum_{i=1}^{m} \left(x_i \left(\frac{\partial Z_{\mathrm{mix}}(T, P, x_1, ..., x_m)}{\partial x_i} \right)_{T, P, x_{i \neq j}} \right) \right)$$

When the system is partially coupled, which means that some but not all species have been coupled, the mixture property is instead calculated assuming ideal mixing:

$$Z_{\mathrm{mix}} = \sum_{i=1}^{m} n_i Z_i(T, P) \tag{2-6}$$

using the pure species properties $Z_i = Z_{\mathrm{mix}}(T, P, x_i = 1, 0, ..., 0)$.

Evaluating a Property Function in a Physics Interface

The functions set up using a thermodynamic system in Thermodynamics can be used directly in any physics interfaces in COMSOL Multiphysics, in the same way as for standard functions. Simply type in the function name with the proper arguments in the appropriate field of the model to use the function. Figure 2-28 shows an example of this from the Reaction Engineering interface. In this example, the **Species Thermodynamic Expressions** section gets input for the molar entropy, the enthalpy and the heat capacity of toluene. These functions, generated using **Species Property** for a thermodynamic system containing toluene, have been entered in the corresponding input fields using the appropriate arguments.
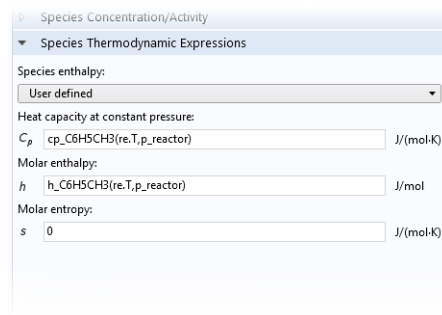
Figure 2-28: The enthalpy and heat capacity of toluene are evaluated using property calculations through a thermodynamics system. In this case, the functions are temperature and pressure dependent properties for a pure component.

User-Defined Species

Use this feature to specify the properties of a new species not available in the included COMSOL database. This feature can also be used to edit a database species, by using an existing species as a template, to create a new one. A User-Defined Species can be included in a Thermodynamic System feature, or Predefined System feature, together with predefined database species and other user-defined species.

The data needed for a user-defined species includes both material properties, such as the molar mass and the vapor pressure, and properties for specific thermodynamic models or transport models (see Thermodynamic Models and Theory). For instance, in order to use the UNIFAC thermodynamic model, you need to define UNIFAC groups for the new species.

Note that the thermodynamics calculator includes measures to handle missing species properties, sometimes by applying approximations. For instance, if the Wilson volume

is not available, the liquid volume at normal boiling point is used instead. If data for this is also missing, it is estimated from the saturated liquid density correlation.

When creating a user-defined species it is recommended to add the following common material properties:

- Molecular mass
- Critical properties
- Acentric factor
- Absolute entropy
- Standard enthalpy of formation
- Ideal gas heat capacity
- Vapor pressure
- Heat of vaporization
- Saturated liquid density
- Transport properties

EXAMPLE MODEL

For an example of using a User-Defined Species see this application example:

	Dissociation in a Tubular Reactor: Application Library path **Chemical_Reaction_Engineering_Module/Thermodynamics/dissociation**

THE USER-DEFINED SPECIES WIZARD

To create a **User-Defined Species**, start the **User-Defined Species Wizard** in one of the following ways:

- Right-click the **Global Definitions** node, select **Thermodynamics** and choose **User-Defined Species**.
- If the model already includes the **Thermodynamics** node, right-click it and choose **User-Defined Species**.
- Using the Reaction Engineering interface, or **Chemistry** interface, choose **User-Defined Species** from the **Thermodynamics** section of the **Reaction Engineering**, or **Chemistry** toolbar.

The **User-Defined Species Wizard** contains the following steps:
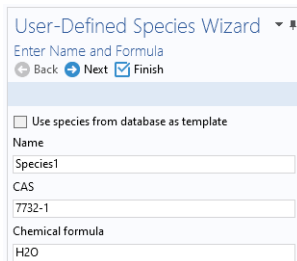
I Enter Name and Formula

2 Enter Parameters

3 Define Properties

ENTER NAME AND FORMULA
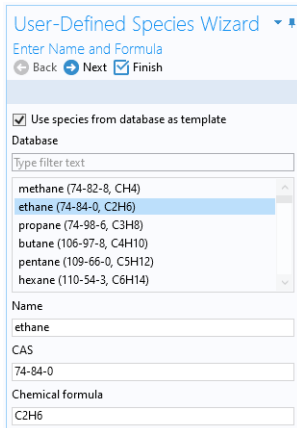
Enter the **Name**, **CAS** number, and the **Chemical formula** for the new species.

Figure 2-29: User-Defined Species Wizard; Enter Name and Formula.

If you want to edit a species in the COMSOL database, select the **Use species from database as template** check box. Then locate the species to edit in the list. The filter text field can be used to search among the available species.

Figure 2-30: User-Defined Species Wizard; edit an available species by selecting Use species from database as template.
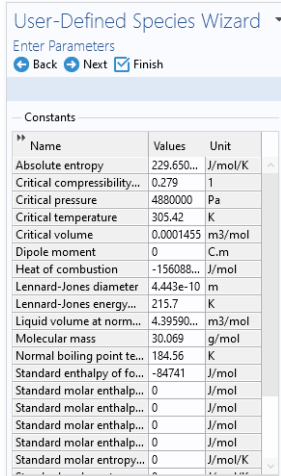
Click the **Next** button ( ) to proceed to the next step.

ENTER PARAMETERS

Define the necessary parameter for the new species.

Constants

Use this table to define material constants such as molar mass, critical temperature, and standard enthalpy of formation.

Figure 2-31: User-Defined Species Wizard; Enter material constants.

Structure information

If you want to use the UNIFAC model, specify the structure formula, the UNIFAC groups and their number occurrences.
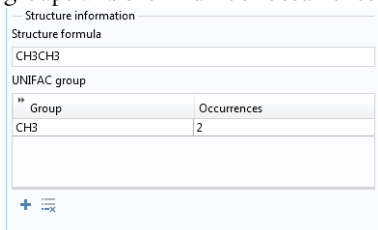
Figure 2-32: User-Defined Species Wizard; Specify the structure information in the Enter Parameters step.

Model parameters

Specify the parameters for the thermodynamic models and transport models in use.

Name	Values	Unit
Chao-Seader acentric factor	0.1064	1
Chao-Seader liquid volume	6.8e-05	m3/mol
Chao-Seader solubility parameter	12379.3085701	J^.5/m^1.5
COSTALAD acentric factor	0.0983	1
COSTALAD volume parameter	0.0001458	m^3/mol
Peng-Robinson Twu L	0.311041	1
Peng-Robinson Twu M	0.866279	1
Peng-Robinson Twu N	1.29869	1
Rackett parameter	0.2808	1
Solubility parameter	13500	J^.5/m^1.5
UNIQUAC Q parameter	1.696	1
UNIQUAC R parameter	1.802	1
Wilson volume parameter	0	m3/mol

Figure 2-33: User-Defined Species Wizard; Specify model parameters.

Click the **Next** button ( ) to proceed to the next step.

DEFINE PROPERTIES

The last step in the wizard is to add temperature dependent properties for the new species. All temperature dependent properties are defined using cubic polynomials on the form

$$f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \tag{2-7}$$

Each property can consist of an arbitrary number of temperature intervals, each using the above form. Click the **Add** button ( ) under the table for a specific property to add an interval.

The following temperature dependent properties are necessary in order to compute the basic set of mixture properties when including the **User-Defined Species** in a thermodynamic system:

- Ideal gas heat capacity
- Liquid density
- Vapor pressure
- Heat of vaporization

Note that some thermodynamic properties, such as the enthalpy and entropy, of a species or mixture, are estimated from the ideal gas heat capacity and depends on the thermodynamic model applied for the system (see Thermodynamic Properties Definitions).

Click the **Finish** button ( ) in the top of the Settings window to finalize the species and add it to the **User-Defined Species** node under **Thermodynamics**.

Figure 2-34: User-Defined Species Wizard; specify temperature-dependent properties.

SETTINGS

Selecting a species node under **User-Defined Species** shows the Settings window including the definitions of all species properties. Properties are categorized into sections as seen in Figure 2-35 below. All properties can be edited by expanding the corresponding section.

> When a species properties has been changed, any **Thermodynamic System** that includes the species needs to be updated for the changes to take effect (see Update From Species).
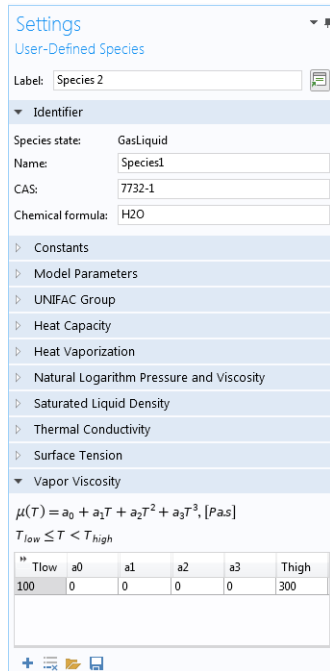
Figure 2-35: The Settings window for a User-Defined Species.

References

1. www.colan.org

2. Cape Open to Cape Open Simulation Environment, www.cocosimulator.org/index_download.html

Thermodynamic Models and Theory

In this section:

Introduction

In this chapter, we review the theory behind the thermodynamic properties database and its functions. The thermodynamic models in the database are available for single phase, gas or liquid, and phase equilibrium systems for two or more phases such as vapor-liquid equilibrium (VLE), vapor-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE).

Thermodynamic Models

In the following sections, the available thermodynamic models are described:

- Equation of State Models
- Liquid Phase Models

EQUATION OF STATE MODELS

An equation of state (EOS) model is an algebraic relation between the absolute pressure (P), the molar volume (V), and the absolute temperature (T). An equation of state that is at least cubic in volume and in the form of

$$Z \equiv \frac{PV}{RT} = f_v(V, T) \tag{2-8}$$

where Z is the compressibility factor and R the universal gas constant, can be used to describe both gases and liquids. The cubic equations of state are widely used to describe the gaseous and liquid volumetric behavior of pure fluids and also all other properties with extensions to mixtures. A comprehensive comparison of different cubic EOS models can be found in Ref. 2 and Ref. 3.

The equations of state models available in the thermodynamic properties database are:

- Ideal Gas Law
- Peng–Robinson
- Peng–Robinson (Twu)
- Soave–Redlich–Kwong
- Soave–Redlich–Kwong (Graboski–Daubert)
- Water (IAPWS)

Ideal Gas Law
The ideal gas law equation of state is

$$P = \frac{RT}{V} \tag{2-9}$$

As the name suggests, the ideal gas law is only applicable to gases. In fact, its use is limited to gases at low to moderate pressures.

Peng–Robinson
The classical Peng–Robinson (PR) equation of state Ref. 5 is given by

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \tag{2-10}$$

where for species i,

$$a_i = \Omega_A \frac{R^2 T_c^2}{P_c} \tag{2-11}$$

$$b_i = \Omega_B \frac{RT_c}{P_c} \tag{2-12}$$

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(4 + 10\Omega_B) \tag{2-13}$$

$$\Omega_B = \left(\beta - \frac{63}{1024\beta} - 0.03125\right) \qquad (2\text{-}14)$$

$$\beta = \left(\frac{351}{32768} + \frac{27}{2048}\sqrt{2}\right)^{\frac{1}{3}} \qquad (2\text{-}15)$$

The alpha function, α_i, is given by

$$\alpha_i = [1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2)(1 - \sqrt{T_{r,\,i}})]^2 \qquad (2\text{-}16)$$

For mixtures

$$a\alpha = \sum_i \sum_j x_i x_j (1 - k_{PR,i,j})\sqrt{(a\alpha)_i (a\alpha)_j} \qquad (2\text{-}17)$$

$$b = \sum_i x_i b_i \qquad (2\text{-}18)$$

The binary interaction parameters (BIPs), k_{PR}, are symmetric with zeros in the diagonal:

$$k_{PR} = k_{PR,i,j} \qquad (2\text{-}19)$$

$$k_{PR,i,j} = 0 \qquad (2\text{-}20)$$

When binary interaction parameters are missing in the database for a set of species, the value is set to zero (a warning node is created). The values for critical temperature, T_c, critical pressure, P_c, and acentric factor, ω_i must be specified for all species.

Peng–Robinson (Twu)
For the Twu modification (Ref. 6) of the Peng–Robinson model, the alpha function, α_i, is replaced by

$$\alpha_i = T + R^{(N_i(M_i - 1))}\exp(L_i(1 - T_{r,\,i}^{N_i M_i})) \qquad (2\text{-}21)$$

The binary interaction parameters k_{PR}, are used for the Twu modification. Acentric factor, ω_i, is not used in this model but critical temperature and critical pressure must be specified for all species. The species specific fit parameters L_i, M_i, N_i can be determined by fitting the pure species phase equilibrium to the vapor pressure curve.

Soave–Redlich–Kwong

The classical Soave–Redlich–Kwong equation of state Ref. 7 is given by

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$$
(2-22)

with

$$\alpha = \frac{1}{\sqrt{T}}$$
(2-23)

and for the pure species i,

$$a_i = \Omega_A \frac{R^2 T_c^{2.5}}{P_c}$$
(2-24)

$$b_i = \Omega_B \frac{RT_c}{P_c}$$
(2-25)

$$\Omega_A = \frac{1}{3} + \frac{1}{3}\Omega_B(3 + 3\Omega_B)$$
(2-26)

$$\Omega_B = \frac{1}{27} 2^{\frac{1}{3}} 27^{\frac{2}{3}} - \frac{1}{3}$$
(2-27)

For mixtures

$$a = \sum_i \sum_j x_i x_j (1 - k_{\mathrm{SRK,i,j}}) \sqrt{a_i a_j}$$
(2-28)

$$b = \sum_i x_i b_i$$
(2-29)

The binary interaction parameters, k_{SRK}, are symmetric with zero in the diagonal:

$$k_{\mathrm{SRK,i,j}} = k_{\mathrm{SRK,j,i}}$$
(2-30)

$$k_{\mathrm{SRK,i,j}} = 0$$
(2-31)

If a value is missing for $k_{\mathrm{SRK},i,j}$ in the database, it is set to zero (a warning node is created). The values for critical temperature, T_c, critical pressure, P_c, and acentric factor, ω_i, must be specified for all species. The Soave–Redlich–Kwong equation of

state is a version of Equation 2-22 modified by Soave Ref. 8, where for pure species i, the alpha function is modified to

$$\alpha_i = [1 + (0.480 + 1.574\omega_i - 0.176\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \qquad (2\text{-}32)$$

Soave–Redlich–Kwong (Graboski–Daubert)
The Graboski and Daubert Ref. 9 modification of the Soave–Redlich–Kwong equation of state replaces alpha function by

$$\alpha_i = [1 + (0.48508 + 1.55174\omega_i - 0.1561\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \qquad (2\text{-}33)$$

except for H_2, where it is replaced by

$$\alpha_{H_2} = 1.202 \exp(-0.30228 T_{r,H_2}) \qquad (2\text{-}34)$$

Water (IAPWS)
The International Association for the Properties of Water and Steam (IAPWS) provides a set of correlations to compute properties of water in different states. The correlations available in COMSOL correspond to the version named Industrial Formulation 1997 (IF-97) Ref. 10 - Ref. 12. The correlations are valid in the following ranges:

$$273.15 \text{ K} \leq T \leq 1073.15 \text{ K} \qquad\qquad p \leq 100 \text{ MPa} \qquad (2\text{-}35)$$

$$1073.15 \text{ K} \leq T \leq 2273.15 \text{ K} \qquad\qquad p \leq 50 \text{ MPa} \qquad (2\text{-}36)$$

The following water and steam properties, available by creating a Species Property, are computed using the IAPWS correlations: density, volume, enthalpy, internal energy, Helmholtz energy, heat capacity at constant pressure, and heat capacity at constant volume. The amounts present in the vapor and liquid phase can be computed using an Equilibrium Calculation.

Other parameters and thermodynamic properties available for the system are provided from the COMSOL database.

LIQUID PHASE MODELS

Activity coefficient models
Activity coefficient models are used to describe liquid mixtures at low to moderate pressures and temperatures where the equations of state are inadequate. When using activity coefficient models, the partial fugacity for species i in the liquid phase is defined as

$$\hat{f}_{i,l} = x_i \gamma_i \phi_{i,sat} P_{i,sat} F_i \qquad (2\text{-}37)$$

which yields

$$\hat{\phi}_{i,l} = \gamma_i \phi_{i,sat} \frac{P_{i,sat}}{P} F_i \qquad (2\text{-}38)$$

where the activity coefficient, γ_i, describes the nonideal liquid phase and $\hat{\phi}_{i,sat} P_{i,sat}$ is the fugacity at the vapor-liquid phase boundary at equilibrium for the pure species i. The Poynting correction, F_i, describes the pure species fugacity deviation from the boiling curve and can be expressed as

$$F_i = \exp\left(\int_{P_{i,sat}}^{P} \frac{V_{i,l}}{RT} dp\right) \qquad (2\text{-}39)$$

For an incompressible liquid, an approximation of the Poynting correction can be done according to

$$F_i \approx \exp\left(\frac{V_{i,l}}{RT}(P - P_{i,sat})\right) \qquad (2\text{-}40)$$

The Poynting correction can often be ignored for moderate pressure. Hence, Equation 2-38 can be expressed as

$$\hat{\phi}_{i,l} = \gamma_i \phi_{i,sat} \frac{P_{i,sat}}{P} \qquad (2\text{-}41)$$

If the vapor phase is considered ideal, then $\phi_{i,sat} = 1$ and the above equation reduces to

$$\hat{\phi}_{i,l} = \gamma_i \frac{P_{i,sat}}{P} \qquad (2\text{-}42)$$

This reduction can be selected explicitly in case the vapor phase is not ideal.

The logarithmic transformation of Equation 2-38 is:

$$\ln \hat{\phi}_{i,l} = \ln \gamma_i + \ln \phi_{i,sat} + \ln P_{i,sat} - \ln P + \ln F_i \qquad (2\text{-}43)$$

Ideal Solution
For an ideal solution the activity coefficient is equal to one, which gives:

$$\ln \gamma_i = 0 \qquad (2\text{-}44)$$

Regular Solution

The Scatchard–Hildebrand equation Ref. 14 for a nonpolar mixture is

$$\ln \gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} \qquad (2\text{-}45)$$

where V_i is species molar volume and δ_i is species solubility parameter, and δ_{av} is

$$\delta_{av} = \frac{\sum_i (x_i V_i \delta_i)}{\sum_i (x_i V_i)} \qquad (2\text{-}46)$$

The volume parameter, V_i, is set equal the liquid volume, $V_{i,l,b}$ at normal boiling point which must be specified for all species. The solubility parameter, δ_i must be specified for all species and can be estimated from the normal heat of vaporization, $\Delta H_{vap,i}$ and the liquid volume at normal boiling point as below:

$$\delta_i \equiv \sqrt{\frac{\Delta H_{vap,i}}{V_{i,l,b}}} \qquad (2\text{-}47)$$

Extended Regular Solution

The extended Scatchard–Hildebrand equation adds the Flory and Huggins correction to the regular solution model Ref. 16:

$$\ln \gamma_i = \frac{V_i(\delta_i - \delta_{av})^2}{RT} + \ln(\theta_i) + 1 - \theta_i \qquad (2\text{-}48)$$

where

$$\theta_i = \frac{V_i}{\sum_i (x_i V_i)} \qquad (2\text{-}49)$$

Wilson

Wilson Ref. 17 derived his activity coefficient model from a consideration of probabilities of neighboring molecules in a liquid

$$\ln \gamma_i = 1 - \sum_j \left(\frac{x_j \Lambda_{j,i}}{\sum_k x_k \Lambda_{j,k}} \right) - \ln \left(\sum_j x_j \Lambda_{i,j} \right) \qquad (2\text{-}50)$$

$$\Lambda_{i,j} = \frac{V_{w,j}}{V_{w,i}} \exp \left(-\frac{\lambda_{i,j}}{T} \right) \qquad (2\text{-}51)$$

where the Wilson volume parameter, $V_{w,i}$, is a species-specific parameter describing volume. If the volume parameter is not available, the liquid volume at normal boiling point is used. The Wilson binary interaction parameters $\lambda_{i,j}$ are specified in terms of absolute temperature. The binary interaction parameter matrix is nonsymmetric and with zeros in its diagonal. All off-diagonal values must be specified

$$\lambda_{i,i} = 0 \qquad (2\text{-}52)$$

$$\Lambda_{i,i} = 1 \qquad (2\text{-}53)$$

NRTL

Renon and Prausnitz (Ref. 18) formulated a three parameter activity coefficient model that is able to describe liquid-liquid equilibrium; the nonrandom two-liquid (NRTL) model:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{j,i} G_{j,i}}{\sum_j x_j G_{j,i}} + \sum_j \left(\frac{x_j G_{j,i}}{\sum_k x_k G_{k,j}} \left(\tau_{i,j} - \frac{\sum_k x_k \tau_{k,j} G_{k,j}}{\sum_k x_k G_{k,j}} \right) \right) \qquad (2\text{-}54)$$

$$\tau_{i,j} = \frac{A_{i,j}}{T} \qquad (2\text{-}55)$$

$$G_{i,j} = \exp(-\alpha_{i,j} \tau_{i,j}) \qquad (2\text{-}56)$$

The three parameters are $A_{i,j}$, $A_{j,i}$, and $\alpha_{i,j}$. A more general form is implemented here:

$$\tau_{i,j} = \frac{A_{i,j}}{T} + B_{i,j} \qquad (2\text{-}57)$$

$$G_{i,j} = \exp(\beta_{i,j} - \alpha_{i,j} \tau_{i,j}) \qquad (2\text{-}58)$$

The binary interaction parameters, $A_{i,j}$, are specified in terms of absolute temperature. The diagonal values are zero and the matrix is nonsymmetric. All off-diagonal values must be specified.

The binary interaction parameters, $B_{i,j}$, have values of zero on the diagonal and the matrix is nonsymmetric. For each pair of species, at least $A_{i,j}$ or $B_{i,j}$ should be specified.

The randomness parameters, $\alpha_{i,j}$, have values of zero on the diagonal and the matrix is symmetric. All off-diagonal values must be specified. Alternatively one can set the more generic form directly specifying parameter $\beta_{i,j}$ for which diagonal values are zero and the matrix is nonsymmetric. For each pair of species at least $\alpha_{i,j}$ or $\beta_{i,j}$ should be specified.

If any value for these parameters is missing in the database, it is set to zero (warning node is created).

$$A_{i,i} = 0 \tag{2-59}$$

$$B_{i,i} = 0 \tag{2-60}$$

$$\alpha_{i,i} = 0 \tag{2-61}$$

$$\alpha_{j,i} = \alpha_{i,j} \tag{2-62}$$

$$\tau_{i,i} = 0 \tag{2-63}$$

$$G_{i,i} = 1 \tag{2-64}$$

$$\beta_{i,i} = 0 \tag{2-65}$$

UNIQUAC

Abrams and Prausnitz followed up with another two-liquid model known as Universal Quasi Chemical equation (UNIQUAC) (see Ref. 19), which is formulated in terms of two activity coefficients:

$$\ln\gamma_i = \ln\gamma_{i,\,\text{comb}} + \ln\gamma_{i,\,\text{res}} \tag{2-66}$$

The first term is the combinatorial part contributes to the Gibbs free energy originating from size and shape effects as

$$\ln\gamma_{i,\,\text{comb}} = 1 - \phi_i + \ln\phi_i - \frac{z}{2}q_i\left(1 + \frac{\phi_i}{\theta_i} + \ln\left(\frac{\phi_i}{\theta_i}\right)\right) \tag{2-67}$$

and the second term is the residual part from chemical interactions between the molecules,

$$\ln\gamma_{i,\,\mathrm{res}} = q_i \left[1 - \ln\left(\frac{\sum\limits_j x_j q_j \tau_{j,\,i}}{\sum\limits_j x_j q_j} \right) - \sum\limits_j \frac{x_j q_j \tau_{j,\,i}}{\sum\limits_k x_j q_j \tau_{k,\,j}} \right] \tag{2-68}$$

where

$$\phi_i = \frac{r_i}{\sum\limits_j x_j r_j} \tag{2-69}$$

$$\theta_i = \frac{q_i}{\sum\limits_j x_j q_j} \tag{2-70}$$

$$\tau_{i,j} = \exp\left(\frac{-\Delta E_{i,j}}{T} \right) \tag{2-71}$$

The coordination number is taken equal to $z = 10$. The binary interaction energy parameters, $\Delta E_{i,j}$, are specified in terms of absolute temperature (K). The diagonal values are zero and the matrix is nonsymmetric. All off-diagonal values must be specified.

$$\Delta E_{i,\,i} = 0 \tag{2-72}$$

$$\tau_{i,\,i} = 1 \tag{2-73}$$

The volume parameters, r_i and surface area parameters, q_i are model-specific parameters for each species. If the parameters are not specified, they can be derived from the van der Waals volume, $V_{\mathrm{VDW},i}$, and area, $A_{\mathrm{VDW},i}$, respectively

$$r_i = \frac{V_{\mathrm{VDW},i}}{0.01517 \cdot 10^{-3}} \tag{2-74}$$

$$q_i = \frac{A_{\mathrm{VDW},i}}{2.5 \cdot 10^{-5}} \tag{2-75}$$

For all species r_i or $V_{\text{VDW},i}$ and q_i or $A_{\text{VDW},i}$ must be specified.

UNIFAC

The UNIQUAC Functional-group Activity Coefficients (UNIFAC; see Ref. 20) uses the same equations as UNIQUAC but the parameters are constructed from group contributions. The model can be used if UNIQUAC parameters are not available for all species. The activity coefficients are calculated from Equation 2-66. The combinatorial part follows from equation Equation 2-67, where

$$r_i = \sum_k \nu_{k,i} r_k \tag{2-76}$$

$$q_i = \sum_k \nu_{k,i} q_k \tag{2-77}$$

where r_k and q_k are the values for group k in species i, and $\nu_{k,i}$ is the number of occurrences of group k in molecule. The residual term in Equation 2-66 is calculated from a summation over functional groups:

$$\ln\gamma_{i,\,\text{res}} = \sum_k \nu_{k,i}(\ln\gamma_{k,\,\text{res}} - \ln\gamma_{i,k,\,\text{res}}) \tag{2-78}$$

The values for $\ln(\gamma_{k,\text{res}})$ are calculated from the mixture containing all species at a specified composition x. The values for $\ln(\gamma_{i,k,\text{res}})$ are calculated for a mixture of group k considering only pure species i. Both are defined, for functional group k, by

$$\ln\gamma_{k,\,\text{res}} = q_k\left(1 - \ln\left(\frac{\sum_l x_l q_l \tau_{l,k}}{\sum_l x_l q_l}\right) - \sum_j \frac{x_l q_l \tau_{k,l}}{\sum_m x_l q_l \tau_{m,l}}\right) \tag{2-79}$$

where x_l and x_m are the compositions of functional group l and m in the mixture

$$x_m = \frac{\sum_i x_i \nu_{m,i}}{\sum_i\left(x_i \sum_k \nu_{k,i}\right)} \tag{2-80}$$

For the calculation of a pure species' i residual activity we get:

$$x_m = \frac{\nu_{m,i}}{\sum\limits_{k} \nu_{k,i}} \tag{2-81}$$

The volume parameters r_k and surface area parameters q_k are model-specific parameters for each group. The binary interaction between groups k and m is

$$\tau_{k,m} = \exp\left(-\frac{A_{k,m}}{T}\right) \tag{2-82}$$

The binary interaction parameters, $A_{k,m}$, are specified in terms of absolute temperature. The diagonal values are zero, the matrix is nonsymmetric. All off-diagonal values must be specified.

The default group and interaction parameters are those published by the UNIFAC consortium (Ref. 21 through Ref. 26), with added groups from Balslev and Abildskov (Ref. 27) but can be modified per package or database. The groups must be specified for all species. Note that the interaction parameter matrix is sparse, and a package can only be used if all interaction parameters for all used groups are specified.

Chao–Seader (Grayson–Streed)
The Chao–Seader model Ref. 13 correlates liquid phase partial coefficients for pure species, for use of hydrogen and hydrocarbon mixtures at elevated pressure and temperatures. It is expressed by

$$\ln\phi_{i,l} = \ln\gamma_i + \ln\phi_{i,l,0} \tag{2-83}$$

The activity is based on the Scatchard–Hildebrand equation Ref. 14 and presented in Equation 2-45 to Equation 2-47. Chao–Seader specific values for liquid volume, V_i and solubility parameter, δ_i are used.

If V_i is unspecified, it can be estimated by

a molar volume at normal boiling point

b van der Waals volume

c from the Rackett model, Equation 2-80, at normal boiling point temperature.

If the Chao–Seader specific solubility parameter, δ_i, is not specified, the generic solubility parameter is used.

The fugacity coefficient for pure species i is correlated as

$$\log\phi_{i,l,0} = \log\phi_{i,l,1} + \omega_i\log\phi_{i,l,2} \tag{2-84}$$

$$\log\phi_{i, l, 1} = A_{i, 0} + \frac{A_{i, 1}}{T_{r, i}} + A_{i, 2}T_{r, i} + A_{i, 3}T_{r, i}^2 + A_{i, 4}T_{r, i}^3 \tag{2-85}$$

$$+(A_{i, 7}T_{r, i}^2 + A_{i, 6}T_{r, i} + A_{i, 5})P_{r, i} + (A_{i, 9}T_{r, i} + A_{i, 8})P_{r, i}^2 - \log P_{r, i}$$

$$\log\phi_{i, l, 2} = A_{i, 10} + \frac{A_{i, 12}}{T_{r, i}} + A_{i, 11}T_{r, i} + A_{i, 13}T_{r, i}^3 + A_{i, 14}(P_{r, i} - 0.6) \tag{2-86}$$

A Chao–Seader specific acentric factor ω_i is used. If it is unknown, it can be set equal to the generic acentric factor. The parameter values are taken from the later publication of Grayson and Streed Ref. 15 and given in Table 2-2.

TABLE 2-2: CHAO–SEADER GRAYSON–STREED FUGACITY COEFFICIENT PARAMETERS.

	H_2	CH_4	OTHER		ALL
$A_{i,0}$	1.50709	1.36822	2.05135	$A_{i,10}$	-4.23893
$A_{i,1}$	2.74283	-1.54831	-2.10899	$A_{i,11}$	8.65808
$A_{i,2}$	-0.02110			$A_{i,12}$	-1.22060
$A_{i,3}$	0.00011	0.02889	-0.19396	$A_{i,13}$	-3.15224
$A_{i,4}$		-0.01076	0.02282	$A_{i,14}$	-0.02500
$A_{i,5}$	0.008585	0.10486	0.08852		
$A_{i,6}$		-0.02529			
$A_{i,7}$			-0.00872		
$A_{i,8}$			-0.00353		
$A_{i,9}$			0.00203		

The corresponding vapor phase model is Redlich–Kwong equation of state. The Chao–Seader (Grayson–Streed) model is valid when

- $255\ \text{K} < T < 533\ \text{K}$
- $P < 6.89\ \text{MPa}$
- $P_r < 0.8$
- $0.5 < T_{r,i} < 1.3$, for all hydrocarbons except CH_4
- $x_{CH4} < 0.3$
- For system that includes CH_4 or H_2S:

$$\sum_i x_i T_{r, i} < 0.93$$

The enthalpy, entropy and Gibbs free energy can be calculated from Equation 2-109 to Equation 2-118.

LIQUID VOLUME MODELS

When an activity coefficient model or the Chao–Seader (Grayson–Streed) model is used, a liquid volume model must be explicitly selected. It is also possible to assign a liquid volume model when an equation of state is used.

For liquids the density is defined as the reciprocal of the liquid volume:

$$\rho_l = \frac{1}{V_l} \tag{2-87}$$

Using a cubic equation of state, the solution has 1, 2, or 3 different roots for the volume. The liquid density is defined as the root producing the highest density, and the vapor density as the root producing the lowest density.

Equation of State

When an equation of state is selected as the liquid phase model, the liquid volume is by default set to be calculated using the same equation of state model. The other liquid volume models; Ideal Mixture, COSTALD, and Rackett are also available.

Note, the vapor phase model and the liquid volume cannot use different equation of state models.

Ideal Mixture

For an ideal mixture the liquid volume is computed from the pure species densities (corresponding to the saturated liquid density):

$$V_{l,m} = \sum_i \frac{x_i}{\rho_{i,l}} \tag{2-88}$$

In this case the pure species densities corresponds to the saturated liquid density, which is available as a temperature dependent correlation for all species in the built-in database.

COSTALD

Hankinson and Thomson Ref. 28 presented the Corresponding States Liquid Density (COSTALD) equation as

$$\frac{V}{V_{mix}} = V_{r,ref}(1 - \omega V_{r,\delta}) \tag{2-89}$$

$$V_{r,ref} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \qquad (2\text{-}90)$$

$$V_{r,\delta} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \qquad (2\text{-}91)$$

$$V_{mix} = \frac{1}{4}\left(\sum_i x_i V_i + 3\left(\sum_i x_i V_i^{2/3} \right)\left(\sum_i x_i V_i^{1/3} \right) \right) \qquad (2\text{-}92)$$

$$T_c = \frac{\left(\sum_i x_i \sqrt{T_{c,i} V_i} \right)^2}{V_{mix}} \qquad (2\text{-}93)$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \ge T_c \end{cases} \qquad (2\text{-}94)$$

$$\omega = \sum_i x_i \omega_i \qquad (2\text{-}95)$$

where the volume, V_i and acentric factor, ω_i for species i are model specific parameters. If the COSTALD volume parameter is unspecified, it is estimated from the van der Waals volume when $V_{VDW,i} > 0.3 \times 10^{-3}$ m^3/mol

$$V_i = 5.385\, V_{VDW,i} - 5.1022 V_{VDW,i}^2 + 79.524 V_{VDW,i}^3 \\ - 99.316 V_{VDW,i}^4 + 100.88 V_{VDW,i}^5 - 1152.7 V_{VDW,i}^6 \qquad (2\text{-}96)$$

otherwise, it can be set equal to the critical volume as

$$V_i = V_{c,i} \qquad (2\text{-}97)$$

If the COSTALD acentric factor, ω_i is not specified, it can be set equal to the generic acentric factor for species i. A critical temperature, $T_{c,i}$ must be specified for all species.

The correlation parameter values are:

TABLE 2-3: REDUCED VOLUME CORRELATION PARAMETERS IN COSTALD.

a	-1.52816	e	-0.296123
b	1.43907	f	0.386914

TABLE 2-3: REDUCED VOLUME CORRELATION PARAMETERS IN COSTALD.

c	-0.81446	g	-0.0427258
d	0.190454	h	-0.0480645

Rackett

The Rackett equation Ref. 29 computes the liquid density at the saturation point, and can be used to describe liquid density at any pressure using the assumption that the liquid is incompressible. The equation and its condition can be expressed as:

$$V_l = \left(R \sum_i \frac{x_i T_{c,i}}{(MW)_i P_{c,i}} \right) \left(\sum_i Z_{r,i} \right)^{(1 + (1 - T_r^2)^{2/7})} \left(\sum_i x_i (MW)_i \right) \tag{2-98}$$

$$T_c = \sum_i x_i T_{c,i} \tag{2-99}$$

$$T_r = \begin{cases} \dfrac{T}{T_c} & T < T_c \\ 1 & T \geq T_c \end{cases} \tag{2-100}$$

Critical temperatures, $T_{c,i}$, critical pressures, $P_{c,i}$, and molecular weights, M_i, must be specified for all species. The model parameter, $Z_{r,i}$, must be specified for all species. If the value is not available it can be set to the critical compressibility factor:

$$Z_{r,i} = Z_{c,i} \tag{2-101}$$

Selecting the Right Thermodynamic Model

Which thermodynamic model is the most appropriate depends on a number of things, for example the nature of the properties to be used, the operational pressure and temperature, and not least the availability of the required model parameters. One general introduction to how to select thermodynamic models, as well as estimating missing parameters and validating properties can be found in Ref. 77.

Below is a decision tree that can be used as a guide for choosing the thermodynamic model:
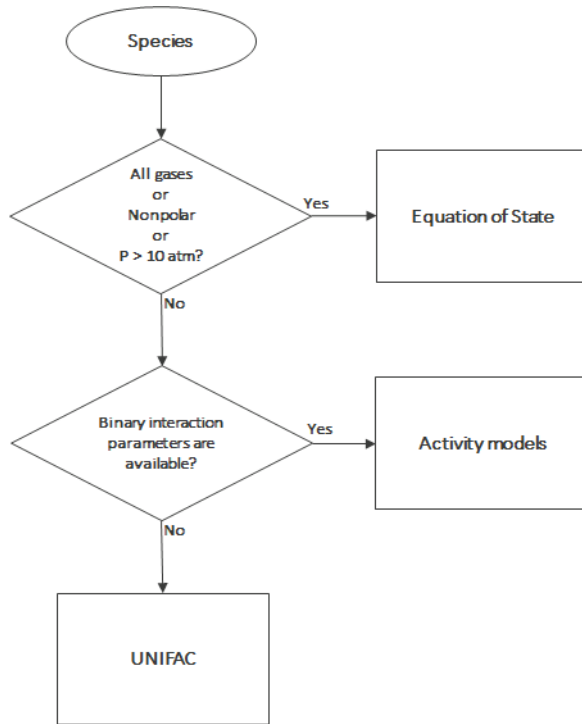
Figure 2-36: Decision tree to select thermodynamics model.

Species Property References

All references used for the included constants and temperature-dependent properties are available in the database file. The reference comments can be inspected in the settings window by right-clicking a species property node (under a **Thermodynamic System**) and selecting **Properties**.

Thermodynamic Properties Definitions

The thermodynamic properties provided are listed as species and mixture property in a Property package.

Ideal Gas

The ideal gas law is independent of composition and determines V at given T and P. Density can be calculated from

$$\rho = \frac{1}{V} \tag{2-102}$$

The partial fugacity coefficients

$$\ln \hat{\phi}_i = 0 \tag{2-103}$$

The ideal gas enthalpy for mixture

$$H_{ig} = \sum_i x_i \left(H_{i,\,ig,\,T_{ref}} + \int_{T_{ref}}^{T} C_{P,\,i,\,ig} dT \right) \tag{2-104}$$

where $H_{i,ig,T\text{ref}}$ relates the enthalpy of an ideal gas to the enthalpy at the selected reference state for species i.

The ideal gas entropy for species i

$$S_{ig} = \sum_i x_i \left(S_{i,\,ig,\,T_{ref}} - R \ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,\,i,\,ig}}{T} dT \right) - R \ln \left(\frac{P}{P_{ref}} \right) \tag{2-105}$$

where $S_{i,ig,T\text{ref}}$ is the entropy of an ideal gas to the entropy of species at the selected reference state.

The Gibbs free energy follows from

$$G_{ig} = H_{ig} - T S_{ig} \tag{2-106}$$

Equation of State

The equation of state determines V at given x, T, and P. Density can be expressed as Equation 2-102. The partial fugacity coefficients are derived from

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_0^P \left(\hat{V}_i - \frac{RT}{P} \right) \tag{2-107}$$

where V_i is the partial molar volume. The enthalpy, entropy, and Gibbs free energy follow from the partial fugacity coefficients and the ideal gas contributions as:

$$H = H_{ig} - RT^2 \sum_i x_i \left(\frac{\partial \ln \hat{\phi}_i}{\partial T} \right) \tag{2-108}$$

$$S = S_{ig} - R \sum_i x_i \left(\ln \hat{\phi}_i + T \frac{\partial \ln \hat{\phi}_i}{\partial T} \right) \tag{2-109}$$

$$G = G_{ig} - RT \sum_i x_i \ln \hat{\phi}_i \tag{2-110}$$

Heat Capacity

Heat capacity at constant pressure is calculated from

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,x} \tag{2-111}$$

It is available when enthalpy is available. Heat capacity at constant volume is defined by

$$C_v = \left(\frac{\partial H}{\partial T} \right)_{v,x} \tag{2-112}$$

The relationship between heat capacity at constant pressure and constant volume can be expressed as:

$$C_p - C_v = T \left(\frac{\partial V}{\partial T} \right)_{P,x} \left(\frac{\partial P}{\partial T} \right)_{v,x} \tag{2-113}$$

were v is a function of T and P. A Taylor expansion of v at constant composition gives

$$\Delta v = \left(\frac{\partial V}{\partial T} \right)_{P,x} \Delta T + \left(\frac{\partial V}{\partial P} \right)_{T,x} \Delta P = 0 \tag{2-114}$$

Rearranging equations above gives

$$C_v = C_P + \frac{T \left(\frac{\partial V}{\partial T} \right)_{P,x}^2}{\left(\frac{\partial V}{\partial P} \right)_{T,x}} \tag{2-115}$$

C_v is available if C_p and volume are available and fluid is compressible by means of volume is pressure dependent. For ideal gas Equation 2-113 express as

$$C_p - C_v = R \tag{2-116}$$

Specific heat capacity ratio is defined as

$$\Upsilon = \frac{C_p}{C_v} \tag{2-117}$$

Activity Coefficient Models

The enthalpy, entropy, and Gibbs free energy follow from the activity coefficients and the ideal gas contributions in Equation 2-104 – Equation 2-106. The activity coefficients describe the deviation of chemical potentials from the ideal liquid phase, so heats of vaporization need to be accounted for

$$H = \sum_i x_i \bigg(H_{i,\,ig,\,T_{ref}} + \int_{T_{ref}}^{T} C_{P,\,i,\,ig} dT - \Delta H_{i,\,vap} - RT^2 \frac{\partial \ln \gamma_i}{\partial T} \tag{2-118}$$
$$- RT^2 \frac{\partial \ln \hat{\phi}_{i,\,sat}}{\partial T} \bigg)$$

$$S = \sum_i x_i \bigg(S_{i,\,ig,\,T_{ref}} - R \ln x_i + \int_{T_{ref}}^{T} \frac{C_{P,\,i,\,ig}}{T} dT - R \ln\bigg(\frac{P_{i,\,sat}}{P_{ref}}\bigg) \tag{2-119}$$
$$+ \ln \gamma_i + T \frac{\partial \ln \gamma_i}{\partial T} + \ln \hat{\phi}_{i,\,sat} + T \frac{\partial \ln \hat{\phi}_{i,\,sat}}{\partial T} + R \frac{\Delta H_{i,\,vap}}{T} \bigg)$$

$$G = \sum_i x_i \bigg(H_{i,\,ig,\,T_{ref}} + \int_{T_{ref}}^{T} C_{P,\,i,\,ig} dT - T \bigg(S_{i,\,ig,\,T_{ref}} + \tag{2-120}$$
$$\int_{T_{ref}}^{T} \frac{C_{P,\,i,\,ig}}{T} dT \bigg) + RT \bigg(\ln x_i + \ln \gamma_i + \ln \hat{\phi}_{i,\,sat} + \ln \frac{P_{i,\,sat}}{P_{ref}} \bigg) \bigg)$$

Note that if the vapor phase is ideal, then the saturated fugacity, $\phi_{i,\,sat}$, contribution can be ignored.

Other Properties

Partial fugacity is calculated from

$$\hat{f}_i = x_i \hat{\phi}_i P \tag{2-121}$$

Internal energy is calculated from

$$U = H - PV + \sum_i x_i U_{i, ig, ref} \qquad (2\text{-}122)$$

where $U_{i,ig,ref}$ is the enthalpy of an ideal gas to the species enthalpy at the selected reference state.

Helmholtz energy is calculated from

$$A = U - TS = G - PV \qquad (2\text{-}123)$$

K-values for phases p and q are taken from

$$K_{i, p, q} = \frac{\hat{\phi}_{i, q}}{\hat{\phi}_{i, p}} \qquad (2\text{-}124)$$

If only liquid phases are defined, the K-value calculation is reduced to

$$K_{i, p, q} = \frac{\gamma_{i, q}}{\gamma_{i, p}} \qquad (2\text{-}125)$$

$$M_{mix} = \sum_i x_i M_i \qquad (2\text{-}126)$$

Standard Enthalpy of Formation and Absolute Entropy Terms

Formation terms are not included in the enthalpy, entropy, or internal energy. If the enthalpy of formation is specified for all species, EnthalpyF (H_F) represent the enthalpy including the formation terms. If the absolute entropy of all species are specified then the EntropyF (S_F) includes the absolute entropy.

At reference conditions, the heat of any reaction relates to the heat of formation as

$$\Delta H_{reac, ref} = \sum_i \nu_i (\Delta H_{f, ref}) \qquad (2\text{-}127)$$

Note that for reacting flow or a heat balance in a reactor when the heat of reaction is explicitly taken into account, the enthalpy should not include the heat of formation.

The following enthalpy expression should be used:

$$H_F = H + \sum_i x_i \Delta H_{f, i, ref} \qquad (2\text{-}128)$$

$H_{f,i,\mathrm{ref}}$ is calculated such that it matches the reference state of the package, even if the species have a different reference state. Similarly, the absolute entropy of each species is taken into account according to

$$S_F = S + \sum_i x_i S_{abs,i} \tag{2-129}$$

The entropy balance over a process that includes reactions should include either the entropy of reaction and use S, or use S_F without entropy of reaction.

In database, a set of parameters introduced to define Absolute entropy and Standard enthalpy of formation for ideal gas and different phases (Vapor, liquid, Solid, and Aqueous infinite dilution). One can use these parameters to calculate Gibbs free energy of reaction when different phases are available (See Electrode reaction).

SPECIES GIBBS FREE ENERGY OF FORMATION

As the COMSOL ThermoDB does not include entropy of formation of species, entropy Equation 2-129 and in consequence Gibbs free energy Equation 2-110 are estimated from absolute entropy's value. Therefore, the absolute value of entropy of formation and Gibbs free energy of formation of the species are not correct. However, for our applications these absolute values are not required while the value of entropy and Gibbs free energy change of reaction (the difference value) are correct.

If user needs the absolute value of entropy of formation, it is possible to estimate it by:

$$S_i = \Delta S_{f,i} = \sum_j \nu_j S_{abs,j} \tag{2-130}$$

where the entropy of formation of species i is calculated from its elemental constituent j. For example, entropy of formation of ammonia at 298 K is

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3 \tag{2-131}$$

$$\Delta S_{f,NH_3} = 2S_{abs,NH_3} - (S_{abs,N_2} + 3S_{abs,H_2}) \tag{2-132}$$

The values from RHS of Equation 2-132 can be extracted from COMSOLThermoDB. This value should be used in Equation 2-128 to estimate the absolute value of Gibbs free energy of species.

Reference State

The reference temperature, pressure and phase can be specified for each package and for species within a package. The reference phase can be a real phase or an ideal gas. If a reference temperature, pressure, or phase is unspecified for a particular species, the package reference temperature, pressure, or phase is used for that species.

The reference values for enthalpy, $H_{i,ref}$, entropy, $S_{i,ref}$, and internal energy, $U_{i,ref}$, are calculated so that the pure species enthalpy, entropy, and internal energy are equal to zero at reference conditions.

The reference values for enthalpy, including formation terms, and entropy, including absolute terms, are calculated such that the corresponding property for pure species i has a value equal to the specified formation term at the species reference conditions.

Transport Properties

This section includes definitions of the models available in for thermal conductivity, viscosity, and diffusivity:

- Thermal Conductivity
- Viscosity
- Diffusivity

THERMAL CONDUCTIVITY

Vapor

Ideal

The thermal conductivity correlations is according to:

$$\lambda_v = \sum_i x_i \lambda_{i,v} + \Delta\lambda_{v,P} \tag{2-133}$$

The pressure correction $\Delta\lambda_{v,P}$ is calculated from the method of Stiel and Thodos, see Ref. 30, which is applicable for $\rho_r < 3$, but is less accurate for H_2, strongly polar gases, and gases with a high degree of hydrogen bonding, such as H_2O and NH_3

$$\Delta\lambda_{v,P} = \frac{P_c^{2/3}}{\sqrt{\bar{M}}T_c^{1/6}Z_c^5}A(\exp((B\rho_r) + C)) \tag{2-134}$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{2-135}$$

$$\rho_c = \frac{1}{V_c} \tag{2-136}$$

The mixing rules are as suggested by Yorizane, see Ref. 31:

$$V_c = \sum_i x_i \sum_j x_j V_{c,i,j} \tag{2-137}$$

$$T_c = \frac{\sum_i x_i \sum_j x_j V_{c,i,j} T_{c,i,j}}{V_c} \tag{2-138}$$

$$\omega = \sum_i x_i \omega_i \tag{2-139}$$

$$Z_c = 0.291 - 0.08\omega \tag{2-140}$$

$$P_c = \frac{RT_c Z_c}{V_c} \tag{2-141}$$

$$M = \sum_i x_i M_i \tag{2-142}$$

where the binary constants are

$$V_{c,i,j} = \frac{1}{8}(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3 \tag{2-143}$$

$$T_{c,i,j} = \sqrt{T_{c,i} T_{c,j}} \tag{2-144}$$

The Stiel and Thodos coefficients are

TABLE 2-4: PRESSURE CORRECTION PARAMETERS.

	A	B	C
$\rho_r < 0.5$	A_1=2.702E8	B_1=0.535	C_1=-1
$0.5 \le \rho_r < 2.0$	A_2=2.528E8	B_2=0.670	C_2=-1.069
$\rho_r \ge 2.0$	A_3=0.574E8	B_3=1.155	C_3= 2.016

However, in order to ensure 0th-order continuity at $\rho_r = 0.5$ and $\rho_r = 2.0$, the following coefficients for $0.5 \leq \rho_r < 2.0$ are recalculated from

$$A_2 = -\frac{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)}{\exp(2.0\ B_2) - \exp(0.5\ B_1)} \tag{2-145}$$

$$
\begin{aligned}
C_2 = &-\frac{A_1 C_1 \exp(2.0\ B_2) + A_1 \exp(0.5\ B_1)\exp(2.0\ B_2)}{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)} \\
&-\frac{A_3 C_3 \exp(2.0\ B_2) + A_3 \exp(0.5\ B_2)\exp(2.0\ B_3)}{A_1 C_1 + A_1 \exp(0.5\ B_1) - A_3 C_3 - A_3 \exp(2.0\ B_3)}
\end{aligned}
\tag{2-146}
$$

The vapor thermal conductivity correlation must be available for all species. Also critical volumes, $V_{c,i}$, critical temperatures, $T_{c,i}$, molecular weights M_i, and acentric factors ω_i must be specified for all species.

Kinetic Theory

Lindsay and Bromley (see Ref. 32) provided an equation for the interaction parameters of the method of Wassiljewa (see Ref. 33) based on the kinetic theory, to provide mixture thermal conductivity from pure species values

$$\lambda_v = \sum_i \left(\frac{x_i \lambda_{i,v}}{\sum_j x_j \phi_{i,j}} \right) + \Delta\lambda_{v,P} \tag{2-147}$$

$$\phi_{i,j} = \frac{1}{4}\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}\left(\frac{M_j}{M_i}\right)^{3/4}\left(\frac{T + \left(\frac{3}{2}\right)T_{b,i}}{T + \left(\frac{3}{2}\right)T_{b,j}}\right)}\right)^2 \left(\frac{T + \sqrt{\left(\frac{9}{4}\right)T_{b,i}T_{b,j}}}{T + \left(\frac{3}{2}\right)T_{b,i}}\right) \tag{2-148}$$

where the pressure correction $\Delta\lambda_{v,P}$ is calculated from Equation 2-134. Both vapor thermal conductivity correlation $\lambda_{i,v}$ and the vapor viscosity correlation $\eta_{i,v}$ must be available for all species. In addition, all normal boiling points $T_{i,b}$, molecular weights M_i, critical volumes $V_{c,i}$, critical temperatures $T_{c,i}$, and acentric factors ω_i must be specified.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 34 which is valid in the following range:

$$273.15 \text{ K} \leq T \leq 773.15 \text{ K} \qquad p \leq 100 \text{ MPa} \qquad (2\text{-}149)$$

$$773.15 \text{ K} \leq T \leq 923.15 \text{ K} \qquad p \leq 70 \text{ MPa} \qquad (2\text{-}150)$$

$$923.15 \text{ K} \leq T \leq 1073.15 \text{ K} \qquad p \leq 40 \text{ MPa} \qquad (2\text{-}151)$$

Liquid

The following mixture models are available for liquid thermal conductivity

Ideal

To calculate the mixture liquid thermal conductivity, $\lambda_{l,m}$, the values of pure liquid thermal conductivity correlations are mixed ideally

$$\lambda_{l,m} = \sum_i x_i \lambda_{i,l} \qquad (2\text{-}152)$$

The pressure dependence is based on the work of Missenard (Ref. 51) where

$$\frac{\lambda_{l,m,P}}{\lambda_{l,m}} = 1 + Q P_r^{0.7} \qquad (2\text{-}153)$$

where Q is correlated as

$$Q = -0.013693477 + 0.057427673 T_r + 0.001617831 (T_r)(\ln P_1) \qquad (2\text{-}154)$$

and the following mixing rules are used

$$T_r = \frac{T}{T_c} \qquad (2\text{-}155)$$

$$P_r = \frac{P}{P_c} \qquad (2\text{-}156)$$

$$P_c = \frac{R T_c Z_c}{V_c} \qquad (2\text{-}157)$$

$$V_c = \sum_i x_i V_{c,i} \qquad (2\text{-}158)$$

$$T_c = \sum_i x_i T_{c,i} \qquad (2\text{-}159)$$

$$Z_c = \sum_i x_i Z_{c,i} \qquad (2\text{-}160)$$

All liquid thermal conductivity correlations must be specified. All values for critical temperatures, $T_{c,i}$, critical volumes, $P_{c,i}$ and critical compressibility factors, $Z_{c,i}$ must be specified for all species i.

Power Law

The values of pure liquid vapor thermal conductivity correlations are mixed according to the following power law

$$\frac{1}{\lambda_{l,m}^2} = \sum_i \frac{x_i}{\lambda_{l,i}} \qquad (2\text{-}161)$$

All liquid thermal conductivity correlations must be specified. The model is valid for pure compound thermal conductivity values that are no more apart than a factor of 2 (Ref. 52 and Ref. 53). The pressure dependence is introduced using Equation 2-153 through Equation 2-160. All values for critical temperatures, $T_{c,i}$, critical volumes, $P_{c,i}$ and critical compressibility factors, $Z_{c,i}$ must be specified for all spices i.

Local Composition

The local composition model by Rowley (Ref. 53) uses an ideal and excess contribution

$$\lambda_{l,m} = \lambda_{l,\,\text{ideal}} + \lambda_{l,\,\text{excess}} \qquad (2\text{-}162)$$

The ideal part is based on mass fractions

$$\lambda_{l,\,\text{ideal}} = \sum_i \omega_i \lambda_{i,l} \qquad (2\text{-}163)$$

$$\omega_i = \frac{x_i M_i}{\sum_j x_j M_j} \qquad (2\text{-}164)$$

The excess term is based on NRTL local concentrations

$$\lambda_{l, \text{excess}} = \frac{\sum_i \sum_j \omega_i \omega_j G_{j,i}(\lambda_{j,i} - \lambda_{i,l})}{\sum_j \omega_j G_{j,i}} \tag{2-165}$$

where $G_{j,i}$ follows from Equation 2-58. The binary interaction terms follow from

$$\lambda_{i,j} = \lambda_{j,i} = \frac{\bar{\omega}_i \bar{\omega}_{i,i} \lambda_{i,l} + \bar{\omega}_j \bar{\omega}_{j,j} \lambda_{j,l}}{\bar{\omega}_i \bar{\omega}_{i,i} + \bar{\omega}_j \bar{\omega}_{j,j}} \tag{2-166}$$

which is symmetric, and on the diagonal,

$$\lambda_{i,i} = \lambda_{i,l} \tag{2-167}$$

and

$$\bar{\omega}_{i,i} = \bar{\omega}_i(\bar{\omega}_i + \bar{\omega}_j G_{j,i}) \tag{2-168}$$

with $\bar{\omega}_i$ is the composition in the binary mixture of species i and j and the local composition is equi-molar

$$\bar{\omega}_i = \frac{M_i \sqrt{G_{j,i}}}{M_i \sqrt{G_{j,i}} + M_j \sqrt{G_{i,j}}} \tag{2-169}$$

All liquid thermal conductivity correlations must be specified. The pressure dependence is introduced using Equation 2-153 – Equation 2-160. All values for critical temperatures $T_{c,i}$, critical volumes $P_{c,i}$, critical compressibility factors $Z_{c,i}$, and molecular weights M_i must be specified for all compounds i. In addition, all NRTL binary interaction parameters $A_{i,j}$ must be specified. Unspecified values for NRTL interaction parameters $B_{i,j}$ are set to zero. The randomness parameters $\alpha_{i,j}$ have values of zero on the diagonal and the matrix is symmetric. All off-diagonal values must be specified. NRTL model is presented in Equation 2-54 to Equation 2-65.

Local Composition (Modified)

Rowley (Ref. 52) adapted the local composition model by replacing the mixing rule in Equation 2-166 by the following

$$\lambda_{i,j} = \lambda_{j,i} = \frac{M_i(\bar{\omega}_i \bar{\omega}_{i,i}) \lambda_{i,l} + M_j(\bar{\omega}_j \bar{\omega}_{j,j}) \lambda_{j,l}}{M_i(\bar{\omega}_i \bar{\omega}_{i,i}) + M_j(\bar{\omega}_j \bar{\omega}_{j,j})} \tag{2-170}$$

which he found to produce better model predictions in most cases where both the Local Composition model and Power Law model have trouble. However, the model is not as generally applicable; for instance, systems containing H_2O are not well described by this model due to the low molecular weight of H_2O.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 34 which is valid in the following range:

$$273.15 \text{ K} \leq T \leq 773.15 \text{ K} \qquad p \leq 100 \text{ MPa} \qquad (2\text{-}171)$$

$$773.15 \text{ K} \leq T \leq 923.15 \text{ K} \qquad p \leq 70 \text{ MPa} \qquad (2\text{-}172)$$

$$923.15 \text{ K} \leq T \leq 1073.15 \text{ K} \qquad p \leq 40 \text{ MPa} \qquad (2\text{-}173)$$

VISCOSITY

Vapor

Wilke

Wilke, see Ref. 35, based his method for mixture viscosity of the vapor phase on kinetic theory:

$$\eta_v = \sum_i \left(\frac{x_i \eta_{i,v}}{\sum_j x_j \Psi_{i,j}} \right) \qquad (2\text{-}174)$$

$$\Psi_{i,j} = \frac{\left(1 + \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \left(\frac{M_j}{Mi} \right)^{1/4} \right)^2}{\sqrt{8 \left(1 + \frac{M_i}{M_j} \right)}} \qquad (2\text{-}175)$$

The vapor viscosity correlation $\eta_{i,v}$ must be available for all species. In addition, all molecular weights M_i must be specified.

Brokaw

Brokaw (see Ref. 36) uses the same basic equation as Wilke (Equation 2-174). However, Equation 2-175 is replaced by

$$\psi_{i,j} = S_{i,j} A_{i,j} \sqrt{\frac{\eta_{i,v}}{\eta_{j,v}}} \tag{2-176}$$

and the interaction parameter is defined as

$$A_{i,j} = \frac{\beta_{i,j}}{\sqrt{RM_{i,j}}} \left(1 + \frac{RM_{i,j} - RM_{i,j}^{0.45}}{2(1 + RM_{i,j}) + \frac{1 + RM_{i,j}^{0.45}}{(\sqrt{\beta_{i,j}})(1 + RM_{i,j})}} \right) \tag{2-177}$$

where

$$\beta_{i,j} = \left(\frac{4 M_i M_j}{(M_i + M_j)^2} \right)^{1/4}, RM_{i,j} = \frac{M_i}{M_j} \tag{2-178}$$

The vapor viscosity correlation, $\eta_{i,v}$ must be available for all species i. In addition, all molecular weights M_i must be specified. If Lennard–Jones energy ε_i (see Ref. 37) Stockmayer's polar parameter $\delta_{s,i}$ (Ref. 38 and Ref. 39) are specified for both species i and j then

$$S_{i,j} = \frac{1 + \sqrt{\frac{T^2}{\varepsilon_i \varepsilon_j}} + \frac{1}{4} \delta_{s,i} \delta_{s,j}}{\sqrt{1 + \frac{T}{\varepsilon_i} + \frac{1}{4} \delta_{s,i}} \sqrt{1 + \frac{T}{\varepsilon_j} + \frac{1}{4} \delta_{s,j}}} \tag{2-179}$$

Otherwise,

$$S_{i,j} = 1 \tag{2-180}$$

Davidson

The Davidson method, see Ref. 40, requires fewer compound specific parameters than Brokaw, while reported accuracy is almost as good, and in the case of H_2, even surpasses it. The Davidson model only requires molar masses and the viscosities of the pure gases. The model is based on fluidity, which is defined to be the reciprocal viscosity.

$$f = \frac{1}{\eta} \tag{2-181}$$

The fluidity of the mixture is then calculated as:

$$f = \sum_{i,j} \left(\frac{y_i y_j}{\sqrt{\mu_i} \sqrt{\mu_j}} \cdot E_{i,j}^A \right) \tag{2-182}$$

where y_i is the momentum fraction of species i, $E_{i,j}$ is the momentum transfer coefficient of the species pair i, j, and A is a empirical species independent parameter set to $1/3$. The momentum fraction is given by:

$$y_i = \frac{x_i \sqrt{M_i}}{\displaystyle\sum_j (x_j \sqrt{M_j})} \tag{2-183}$$

and the momentum transfer coefficient is taken as:

$$E_{i,j} = \frac{2 \sqrt{M_i} \sqrt{M_j}}{M_i + M_j} \tag{2-184}$$

High Pressure Modification

To account for the effect of pressure on vapor viscosity, a pressure correction can be applied. The pressure dependence is based on kinetic gas theory, which adds the following term to the vapor viscosity:

$$\Delta \eta_{v, P} = \left(\frac{\sqrt{M_t} P_c^{2/3}}{T_c^{1/6}} \right) \left(\frac{10^{-7}}{101325^{2/3}} \zeta \right) \tag{2-185}$$

where ξ is calculated from the correlation of Jossi (Ref. 41), which is applicable for $\rho_r < 3.0$. It is less accurate for H_2, strongly polar gases and gases with a high degree of hydrogen bonding such as H_2O and NH_3.

The correction factor is due to using pressure, atm, and viscosity, cP, units in Jossi's correlation. It is expressed as:

$$(\xi + 1)^{\frac{1}{4}} = 1.0230 + 0.23364 \rho_r + 0.58533 \, \rho_r^2 \tag{2-186}$$

$$- 0.40758 \, \rho_r^3 + 0.093324 \, \rho_r^4$$

$$\rho_r = \frac{\rho}{\rho_c} \tag{2-187}$$

$$\rho_c = \frac{1}{V_c} \tag{2-188}$$

The following mixture rules are used

$$P_c = \frac{RT_cZ_c}{V_c}, \; V_c = \sum_i x_iV_{c,i}, \; T_c = \sum_i x_iT_{c,i} \tag{2-189}$$

$$Z_c = \sum_i x_iZ_{c,i}, \; M_t = \sum_i x_iM_i \tag{2-190}$$

The values for critical volumes, $V_{c,i}$, critical temperatures, $T_{c,i}$, critical compressibility factors, $Z_{c,i}$ and molecular weights, M_i must be specified for all species i.

The high pressure correction is available for the Wilke, Brokaw, and Davidson mixture models. The vapor viscosity follows from

$$\eta_v = \eta_{v,\text{Wilke}} + \Delta\eta_{v,P} \tag{2-191}$$

where $\eta_{v,\text{Wilke}}$ is calculated from Equation 2-174.

Pedersen Corresponding States Model

The corresponding states viscosity model of Pedersen (Ref. 42 and Ref. 43) applies to both vapor and liquid phases of hydrocarbon mixtures. The selected reference species is CH_4.

The CH_4 viscosity is calculated from Ref. 44, modified by Pedersen and Fredenslund (Ref. 45) to avoid issues below 91 K where CH_4 becomes solid

$$\eta_{CH_4} = \eta_{CH_4,0} + \rho_{CH_4}\eta_{CH_4,1} + F_1\eta_{CH_4,2} + F_2\eta_{CH_4,3} \tag{2-192}$$

where

$$F_1 = \frac{H+1}{2} \tag{2-193}$$

$$F_1 = \frac{1-H}{2} \tag{2-194}$$

$$H = \frac{\exp(\Delta T) - \exp(-\Delta T)}{\exp((\Delta T) + \exp(-\Delta T))} \tag{2-195}$$

$$\Delta T = T - 91 \text{ K} \qquad (T \in K) \tag{2-196}$$

Here, ρ_{CH4} is used in g/cm^3; for the mass-mole conversion of ρ_{CH4}, a molecular weight of $M_{CH4} = 16.042568$ g/mol is used.

The dilute gas part is given by

$$\eta_{CH_4,0} = \frac{-L_1}{T} + \frac{L_2}{T^{2/3}} - \frac{L_3}{T^{1/3}}$$
$$+ L_4 - L_5 T^{1/3} + L_6 T^{2/3} - L_7 T + L_8 T^{4/3} - L_9 T^{5/3}$$

(2-197)

The first density correction for the moderately dense gas is given by

$$\eta_{CH_4,1} = L_{10} - L_{11}\left(1.4 - \ln\frac{T}{168 \text{ K}}\right)^2$$

(2-198)

The remainder is given by the empirical correlation

$$\eta_{CH_4,2} = \exp\left(\frac{L_{12}}{T} - L_{13}\right)\left(\exp\left[\left(\sqrt[10]{\rho_{CH_4}}\right)\left(L_{14} - \frac{L_{15}}{T^{3/2}}\right) + \right.\right.$$
$$\left.\left.\left(\frac{\rho_{CH_4} - \rho_{c,CH_4}}{\rho_{c,CH_4}}\right)\left(\sqrt{\rho_{CH_4}}\right)\left(L_{16} + \frac{L_{17}}{T} + \frac{L_{18}}{T^2}\right)\right] - 1\right)$$

(2-199)

The correction term for solid CH_4

$$\eta_{CH_4,3} = \exp\left(\frac{L_{19}}{T} - L_{20}\right)\left(\exp\left[\left(\sqrt[10]{\rho_{CH_4}}\right)\left(L_{21} - \frac{L_{22}}{T^{3/2}}\right)\right.\right.$$
$$\left.\left. + \left(\frac{\rho_{CH_4} - \rho_{c,CH_4}}{\rho_{c,CH_4}}\right)\left(\sqrt{\rho_{CH_4}}\right)\left(L_{23} + \frac{L_{24}}{T} + \frac{L_{25}}{T^2}\right)\right] - 1\right)$$

(2-200)

with the values of the parameters L_1 through L_{25} are listed in Table 2-5 below:

TABLE 2-5: METHANE VISCOSITY NUMERICAL COEFFICIENTS.

L_1	$2.090975 \cdot 10^5$	L_{10}	1.696985927	L_{19}	9.74602
L_2	$2.647269 \cdot 10^5$	L_{11}	0.133372346	L_{20}	44.6055
L_3	$1.472818 \cdot 10^5$	L_{12}	188.73011594	L_{21}	18.0834
L_4	47167.40	L_{13}	10.35060586	L_{22}	4126.66
L_5	9491.827	L_{14}	17.571599671	L_{23}	0.976544
L_6	1219.979	L_{15}	3019.3918656	L_{24}	81.8134
L_7	96.27993	L_{16}	0.042903609488	L_{25}	15649.9

TABLE 2-5: METHANE VISCOSITY NUMERICAL COEFFICIENTS.

L_8	4.274152	L_{17}	145.29023444		
L_9	0.08141531	L_{18}	6127.6818706		

Here, ρ_{CH4} is used in g/cm^3; the critical density is given by $\rho_{c,CH4} = 0.16284$ g/cm^3. The following equation by McCarty (Ref. 46) is solved for the density of CH_4

$$P = N_1\rho_{CH_4}T + \rho_{CH_4}^2\left(-N_2T + N_3\sqrt{T} - N_4 + \frac{N_5}{T} - \frac{N_6}{T^2}\right) \qquad (2\text{-}201)$$

$$+ \rho_{CH_4}^3\left(N_7T - N_8 + \frac{N_9}{T} - \frac{N_{10}}{T^2}\right) + \rho_{CH_4}^4\left(-N_{11}T + N_{12} + \frac{-N_{13}}{T}\right) + N_{14}\rho_{CH_4}^5$$

$$+ \rho_{CH_4}^6\left(-\frac{N_{15}}{T} + \frac{N_{16}}{T^2}\right) + N_{17}\frac{\rho_{CH_4}^7}{T} + \rho_{CH_4}^8\left(\frac{N_{18}}{T} + \frac{N_{19}}{T^2}\right) + N_{20}\frac{\rho_{CH_4}^9}{T}$$

$$+ \exp(-N_{21}\rho_{CH_4}^2)\left(\rho_{CH_4}^3\left(\frac{N_{22}}{T^2} - \frac{N_{23}}{T^3}\right) + \rho_{CH_4}^5\left(\frac{N_{24}}{T^2} + \frac{N_{25}}{T^4}\right) + \rho_{CH_4}^7\left(\frac{N_{26}}{T^2} + \frac{N_{27}}{T^3}\right)\right.$$

$$\left. + \rho_{CH_4}^9\left(-\frac{N_{28}}{T^2} - \frac{N_{29}}{T^4}\right) + \rho_{CH_4}^{11}\left(-\frac{N_{30}}{T^2} + \frac{N_{31}}{T^3}\right) + \rho_{CH_4}^{13}\left(\frac{N_{32}}{T^2} - \frac{N_{33}}{T^3} + N_{34}T^4\right)\right)$$

where ρ_{CH4} is used in mol/l.

TABLE 2-6: COEFFICIENTS IN THE FUNCTIONAL FORM OF THE MCCARTY EOS.

N_1	0.08205616	N_{13}	2.8685285973	N_{25}	$1.6428375992 \cdot 10^6$
N_2	0.018439486666	N_{14}	$0.11906973942 \cdot 10^{-3}$	N_{26}	0.21325387196
N_3	1.0510162064	N_{15}	0.0085315715699	N_{27}	37.791273422
N_4	16.057820303	N_{16}	3.8365063841	N_{28}	$0.1185701681 \cdot 10^{-4}$
N_5	848.44027562	N_{17}	$0.24986828379 \cdot 10^{-4}$	N_{29}	31.630780767
N_6	42738.409106	N_{18}	$0.57974531455 \cdot 10^{-5}$	N_{30}	$0.4100678294 \cdot 10^{-5}$
N_7	$0.76565285254 \cdot 10^{-3}$	N_{19}	0.0071648329297	N_{31}	0.0014870043284
N_8	0.48360724197	N_{20}	$0.12577853784 \cdot 10^{-3}$	N_{32}	$3.151226153 \cdot 10^{-9}$
N_9	85.195473835	N_{21}	0.0096	N_{33}	$0.2167077474 \cdot 10^{-5}$
N_{10}	16607.434721	N_{22}	22240.102466	N_{34}	$0.2400055107 \cdot 10^{-4}$
N_{11}	$0.37521074532 \cdot 10^{-4}$	N_{23}	$1.4800512328 \cdot 10^6$		
N_{12}	0.028616309259	N_{24}	50.498054887		

With the viscosity and density of CH_4 defined, the viscosity of any mixture, η_m, can be calculated from the corresponding states principle

$$\eta_m = \left(\frac{T_c}{T_{c,\,CH_4}}\right)^{\frac{-1}{6}}\left(\frac{P_c}{P_{c,\,CH_4}}\right)^{2/3}\left(\frac{M_m}{M_{CH_4}}\right)^{1/2}\left(\frac{\alpha}{\alpha_{CH_4}}\right)\eta_{CH_4,\,P_0,\,T_0} \qquad (2\text{-}202)$$

where the CH_4 viscosity $\rho_{CH4,P0,T0}$ is calculated at temperature T_0 and pressure P_0:

$$T_0 = \left(\frac{T_{c,\,CH_4}}{Tc}\right)T\left(\frac{\alpha_{CH_4}}{\alpha}\right) \qquad (2\text{-}203)$$

$$P_0 = \left(\frac{P_{c,\,CH_4}}{Pc}\right)P\left(\frac{\alpha_{CH_4}}{\alpha}\right) \qquad (2\text{-}204)$$

The following mixing rules are used for the critical properties, see :

$$T_c = \frac{\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\sqrt{T_{c,\,i}T_{c,\,j}}}{\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}} \qquad (2\text{-}205)$$

$$P_c = \frac{8\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\sqrt{T_{c,\,i}T_{c,\,j}}}{\left(\displaystyle\sum_i\sum_j x_i x_j \beta_{i,j}\right)^2} \qquad (2\text{-}206)$$

$$\beta_{i,j} = \left(\left(\frac{T_{c,\,i}}{P_{c,\,i}}\right)^{1/3} + \left(\frac{T_{c,\,j}}{P_{c,\,j}}\right)^{1/3}\right)^3 \qquad (2\text{-}207)$$

The parameter α is

$$\alpha = 1 + 7.378\times10^{-3}\rho_r^{1.847}M_m^{0.5173} \qquad (2\text{-}208)$$

$$\rho_r = \frac{\rho_{CH_4,\,\bar{P}_0,\,\bar{T}_0}}{\rho_{c,\,CH_4}} \qquad (2\text{-}209)$$

where

$$\bar{T}_0 = \left(\frac{T_{c,\,CH_4}}{Tc}\right)T \qquad (2\text{-}210)$$

$$\bar{P}_0 = \left(\frac{P_{c,\,CH_4}}{Pc}\right)P \tag{2-211}$$

with $\rho_{c,CH4} = 0.16284$ g/cm^3. For CH_4

$$\alpha_{CH_4} = 1 + 7.378 \times 10^{-3} \rho_r^{1.847} M_{CH_4}^{0.5173} \tag{2-212}$$

where Equation 2-209 is used. The mixture molecular weight is a function of the weight-averaged molecular weight and the number-averaged molecular weight

$$M_m = 1.304 \times 10^{-4} (M_W^{2.303} - M_N^{2.303}) + M_N \tag{2-213}$$

$$M_W = \frac{\sum_i x_i M_i^2}{M_N} \tag{2-214}$$

$$M_N = \sum_i x_i M_i \tag{2-215}$$

where the power in Equation 2-213 is determined by fitting to experimental viscosity data.

Note that pure species vapor viscosity correlations $\eta_{i,v}$ are not required. However, for each species i, molecular weight M_i, critical temperature, $T_{c,i}$, and critical pressure, $P_{c,i}$ must be specified.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 48–Ref. 49 for industrial application which is valid in the following range:

$$273.16 \text{ K} \le T \le 1173.15 \text{ K} \qquad 0 \le p \le p_t \tag{2-216}$$

$$T_m(p) \le T \le 1173.15 \text{ K} \qquad p_t \le p \le 300 \text{ MPa} \tag{2-217}$$

$$T_m(p) \le T \le 873.15 \text{ K} \qquad 300 \text{ MPa} \le p \le 350 \text{ MPa} \tag{2-218}$$

$$T_m(p) \le T \le 433.15 \text{ K} \qquad 350 \text{ MPa} \le p \le 500 \text{ MPa} \tag{2-219}$$

$$T_m(p) \le T \le 373.15 \text{ K} \qquad 500 \text{ MPa} \le p \le 1000 \text{ MPa} \tag{2-220}$$

where T_m is the pressure dependent melting temperature and p_t is the triple-point pressure. In accordance with industrial application recommendations, critical region correction is not applied.

Liquid

The following mixture models are available for liquid viscosity.

Molar Logarithmic Mixing

The values of pure species log liquid viscosity, $\ln \eta_{i,l}$ are mixed ideally using mole fractions x_i

$$\ln \eta_{l,m} = \sum_i x_i \ln \eta_{i,l} \qquad (2\text{-}221)$$

where $\eta_{m,l}$ is the mixture viscosity of liquids.

Mass Logarithmic Mixing

The values of pure species log liquid viscosity correlation are mixed ideally using the weight fractions ω_i

$$\ln \eta_{l,m} = \sum_i \omega_i \ln \eta_{i,l} \qquad (2\text{-}222)$$

Pedersen Corresponding States Model

The Pedersen Corresponding States Model described above for the gas phase viscosity also applies to the liquid phase. Pure species liquid viscosity correlations are not required. However, for each species i, molecular weight M_i, critical temperature $T_{c,i}$, and critical pressure $P_{c,i}$, must be specified.

Cubic mixing

The mixture viscosity is defined using the cubic root average in terms of the mole fractions x_i

$$\eta_{l,m} = \left(\sum_i x_i \eta_{i,l}^{1/3} \right)^3 \qquad (2\text{-}223)$$

The model is noted in Ref. 50 to provide reasonable results for hydrocarbon mixtures of similar components.

The model requires that the log liquid viscosity correlation is available for all species i.

Cubic mass mixing

The mass fraction equivalent of the previous model is

$$\eta_{l,m} = \left(\sum_i \omega_i \eta_{i,l}^{1/3}\right)^3 \qquad (2\text{-}224)$$

The model requires that the log liquid viscosity correlation is available for all species i.

Water (IAPWS)

The International Association of the Properties of Water and Steam recommend an equation Ref. 48–Ref. 49 for industrial application which is valid in the following range:

$$273.16\text{K} \leq T \leq 1173.15\text{K} \qquad 0 \leq p \leq p_t \qquad (2\text{-}225)$$

$$T_m(p) \leq T \leq 1173.15 \text{ K} \qquad p_t \leq p \leq 300 \text{ MPa} \qquad (2\text{-}226)$$

$$T_m(p) \leq T \leq 873.15 \text{ K} \qquad 300 \text{ MPa} \leq p \leq 350 \text{ MPa} \qquad (2\text{-}227)$$

$$T_m(p) \leq T \leq 433.15 \text{ K} \qquad 350 \text{ MPa} \leq p \leq 500 \text{ MPa} \qquad (2\text{-}228)$$

$$T_m(p) \leq T \leq 373.15 \text{ K} \qquad 500 \text{ MPa} \leq p \leq 1000 \text{ MPa} \qquad (2\text{-}229)$$

where T_m is the pressure dependent melting temperature and p_t is the triple-point pressure. In accordance with industrial application recommendations, critical region correction is not applied.

DIFFUSIVITY

Two types of diffusion coefficients are supported. Diffusion coefficients in infinitely diluted systems, and Maxwell–Stefan diffusion coefficients.

For dilute systems, the binary diffusion coefficient $D^0_{i,j}$ represent the diffusivity of species i in a medium consisting of pure species j. This corresponds to the Fickian diffusion coefficient.

For any mixture, the binary Maxwell–Stefan diffusion coefficient $\mathcal{D}_{i,j}$, represents the inverse drag coefficient of species i moving past species j (Ref. 54–Ref. 57). This

property is referred to as the Maxwell–Stefan diffusivity. The Maxwell–Stefan diffusivity is symmetric, $Ð_{i,j} = Ð_{j,i}$, and the diagonal elements $Ð_{i,i}$ are not used.

Gas Phase Diffusion Coefficient at Infinite Dilution

The following models are available for the diffusion coefficients at infinite dilution in the vapor phase:

- Fuller–Schettler–Giddings
- Wilke–Lee

Automatic When the Gas diffusivity property model is set to Automatic, the Fuller–Schettler–Giddings model is used, provided that the Fuller diffusion volume is known for both species (i and j), otherwise the Wilke–Lee model is used.

Fuller–Schettler–Giddings

Fuller and others (Ref. 58) modified the Chapman–Enskog relation to correlate binary diffusion coefficient for species i and j in the vapor phase according to the Fuller–Schettler–Giddings (FGS) model:

$$D_{i,j}^0 = \frac{1.01325 \times 10^{-2} T^{1.75} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P\left(\left(\sum_i v\right)^{\frac{1}{3}} + \left(\sum_j v\right)^{\frac{1}{3}}\right)^2} \tag{2-230}$$

where T denotes the temperature (K), M_i the molecular weight of species i (g/mol) and P is the pressure (Pa). v_i are the atomic diffusion volumes (Fuller diffusion volume, cm^3), which are estimated using group contribution for each species (Ref. 59):

TABLE 2-7: ATOMIC AND STRUCTURAL DIFFUSION VOLUME INCREMENTS

GROUP	CONTRIBUTION
C	15.9
H	2.31
O	6.11
N	4.54
F	14.7
Cl	21
Br	21.9

TABLE 2-7: ATOMIC AND STRUCTURAL DIFFUSION VOLUME INCREMENTS

GROUP	CONTRIBUTION
I	29.8
S	22.9
Aromatic Ring	-18.3
Heterocyclic Ring	-18.3

For some simple molecules the values below, determined from regression, are used:

TABLE 2-8: DIFFUSION VOLUMES OF ATOM AND SIMPLE MOLECULES

SPECIES	FULLER DIFFUSION VOLUME
He	2.67
Ne	5.98
Ar	16.2
Kr	24.5
Xe	32.7
H_2	6.12
D_2	6.84
N_2	18.5
O_2	16.3
CO	18
CO_2	26.9
N_2O	35.9
NH_3	20.7
H_2O	13.1
SF_6	71.3
Cl_2	38.4
Br_2	69
SO_2	41.8
Air	19.7

Wilke–Lee

Wilke and Lee (Ref. 60) also modified the Chapman–Enskog relation to correlate
binary diffusion coefficient in vapor phase according to:

$$D_{i,j}^0 = 10^{-2} \times \frac{3.03 - \left(\dfrac{0.98}{\sqrt{MW_{i,j}}}\right)T^{1.5}}{P\sigma_{i,j}^2\Omega_D\sqrt{MW_{i,j}}} \tag{2-231}$$

where

$$MW_{i,j} = \frac{2}{\dfrac{1}{M_i} + \dfrac{1}{M_j}} \tag{2-232}$$

The length scale $\sigma_{i,j}$ for the interaction is taken from the Lennard–Jones diameter parameters of species i and j:

$$\sigma_{i,j} = \frac{(\sigma_i^{LJ} + \sigma_j^{LJ})}{2} \tag{2-233}$$

If σ_i^{LJ} is not specified in the database, it is instead estimated from:

$$\sigma_i^{LJ} = 1.18 \times 10^{-8} V_{i,l,b}^{\frac{1}{3}} \tag{2-234}$$

where $V_{i,l,b}$ is the molar volume of species at normal boiling point.

The collision integral Ω_D is evaluated from (Ref. 61):

$$\Omega_D = 1.06036\, T^{*-0.15610} + 0.19300\, \exp\,(-0.47635\, T^*) \tag{2-235}$$
$$+\, 1.03587\, \exp\,(-1.52996\, T^*) + 1.76474\, \exp\,(-3.89411\, T^*)$$

with

$$T^* = \frac{T}{\varepsilon_{i,j}} \tag{2-236}$$

The energy scale $\varepsilon_{i,j}$ for the interaction is taken from the Lennard–Jones energy parameters of species i and j:

$$\varepsilon_{i,j} = \sqrt{\varepsilon_i^{LJ}\varepsilon_j^{LJ}} \tag{2-237}$$

If ε_i^{LJ} is not specified in the database, it is instead estimated from:

$$\frac{\varepsilon_i^{LJ}}{k} = 1.15\, T_{i,l,b} \tag{2-238}$$

where k is the Boltzmann constant and $T_{i,l,b}$ is the normal boiling point temperature.

Gas Phase Maxwell–Stefan Diffusivity

For gas phase diffusion the Maxwell–Stefan diffusivities are defined from the models for gas phase diffusivity at infinite dilution

$$\mathcal{D}_{i,j} = D^0_{i,j} \qquad\qquad (i \neq j) \qquad\qquad\qquad (2\text{-}239)$$

All models for gas phase diffusion at infinite dilution are symmetric, the diffusivity of species i in species j equals that of species j in species i. In addition, under the ideal gas assumption, the Maxwell–Stefan diffusion coefficient matches the Fick diffusion coefficient. This implies that the Maxwell–Stefan gas diffusivities provided are independent of composition.

Liquid Phase Diffusion Coefficients at Infinite Dilution

The following models are available for the diffusion coefficients at infinite dilution in liquid phase:

- Wilke–Chang
- Tyn–Calus
- Hayduk–Minhas
- Siddiqi–Lucas
- Erkey–Rodden–Akgerman

Automatic When the Liquid diffusivity at infinite dilution property model is set to Automatic, a selection for each solute i in solvent j will be made from the models according to the following rules. Except in the case of a temperature correlation and the Erkey–Rodden–Akgerman model, all of these rules require that the log liquid viscosity correlation, $\ln \eta_j$ is available in the database for species j and that the liquid volume at normal boiling point, $V_{i,l,b}$ is available for the species i.

- If a temperature correlation is available for species i and j, it is used.
- If the solvent is water, the Siddiqi–Lucas correlation (for aqueous systems) is used.
- If the solute and solvent are both normal paraffins, the Hayduk–Minhas correlation (for normal paraffins) is used.
- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the solute is hydrogen, carbon-monoxide or carbon-dioxide, the Erkey–Rodden–Akgerman correlation (for normal paraffins) is used.

- If parachors P_i and P_j are both available, and the liquid volume at normal boiling point, $V_{i,l,b}$ is available for the solvent, the Tyn–Calus correlation is used.

- If parachors P_i and P_j are both available, the Hayduk–Minhas correlation is used.

- If the solute and solvent are both organic molecules and the liquid volume at normal boiling point, $V_{i,l,b}$ is available for the solvent, the Siddiqi–Lucas method is used.

- If the molecular weight M_j is available for the solvent, the Wilke–Chang correlation is used.

- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the solute is a normal paraffin, the Erkey–Rodden–Akgerman correlation (for normal paraffins) is used.

- If the solvent is a normal paraffin, and the liquid density correlation for the solvent is available, and the Lennard–Jones diameter for the solute is available, the Erkey–Rodden–Akgerman correlation (for normal paraffins) is used.

For the Siddiqi–Lucas method, a molecule is considered organic if it has at least one C atom bound to anything other than O or C atoms. This is determined by the SMILES formula, if available. If, for any pair of species, the required input data for none of the above models is available, the entire property liquid diffusion coefficient at infinite dilution is not available.

Wilke–Chang

The correlation by Wilke and Chang (Ref. 62) for liquid phase diffusion coefficients at infinite dilution is:

$$D_{i,j}^0 = 1.858795959 \times 10^{-18} \frac{T \sqrt{\phi_j M_j}}{\eta_j V_{i,l,b}^{0.6}} \tag{2-240}$$

Molecular weight, M_j and log liquid viscosity correlation, $\ln \eta_j$, for species j and liquid molar volume at normal boiling point for species i, $V_{i,l,b}$, is required. The Wilke-Chang association parameter ϕ_j, if unavailable, is set to:

TABLE 2-9: ASSOCIATION PARAMETERS FOR SOLVENT

SOLVENT	ASSOCIATION PARAMETER
Water	2.26 (Ref. 63)
Methanol	1.9
Ethanol	1.5
Others	1

Species are identified by their CAS number or SMILES formula. The Wilke–Chang correlation is not suitable for diffusion of water. If water is the solute, the correction suggested by Kooijman (Ref. 64) is applied where liquid molar volume of water at normal boiling point, $V_{\text{water},l,b}$ is multiplied by 4.5.

Tyn–Calus

The Correlation by Tyn and Calus (Ref. 65) for liquid diffusion coefficients at infinite dilution reads:

$$
D_{i,j}^0 \;=\; 8.93 \times 10^{-16} \frac{T\!\left(V_{i,l,b}^{\frac{1}{6}}\right)P_j^{0.6}}{\eta_j\!\left(V_{j,l,b}^{\frac{1}{3}}\right)P_i^{0.6}}
\tag{2-241}
$$

The log liquid viscosity correlation $\ln \eta_j$ should be available for species j, The liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i should be available for both species i and j.

If the solvent is nonpolar (dipole moment is zero), and the solvent is methanol, ethanol or 1-butanol or if the solvent is a mono-hydroxy alcohol, both the liquid volume at normal boiling point, $V_{j,l,b}$ and the parachor, P_j are corrected by a factor of $8 \times 10^3 \eta_j$.

If the solute is water, both the liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i for the solute are corrected by a factor 2. This factor also applies if it is detected from the SMILE formula that the species is an organic acid (a carboxyl group is found), except in the cases where the solvent is water, methanol or n-butanol.

Hayduk–Minhas

Hayduk and Minhas (Ref. 66) suggested three different correlations for liquid diffusion coefficients at infinite dilution.

Aqueous Solutions: in case the solvent is water (derived from CAS number or SMILES formula), the correlation reads:

$$D_{i,j}^0 = 1.25 \times 10^{-12} T^{1.52} \left(\frac{0.07244359601}{V_{i,l,b}^{0.19}} - 0.292 \right) \tag{2-242}$$

$$\times (\eta_j \times 10^3)^{\left(\frac{9.58 \times 10^{-6}}{V_{i,l,b}} - 1.12 \right)}$$

Normal paraffin solutions: In case both the solute and solvent are normal paraffins (derived from SMILES formula), the correlation reads:

$$D_{i,j}^0 = 7.30889362 \times 10^{-16} T^{1.47} \left(\frac{(\eta_j \times 10^3)^{\left(\frac{10.2 \times 10^{-6}}{V_{i,l,b}} - 0.791 \right)}}{V_{i,l,b}^{0.71}} \right) \tag{2-243}$$

For all other systems, the correlation is:

$$D_{i,j}^0 = 3.8934239 \times 10^{-16} \frac{T^{1.29} \sqrt{P_j}}{\eta_j^{0.92} (V_{j,l,b}^{0.23}) P_i^{0.42}} \tag{2-244}$$

If the solvent is nonpolar (dipole moment is zero), and the solvent is methanol, ethanol or 1-butanol or if the solvent is a mono-hydroxy alcohol, both the liquid volume at normal boiling point, $V_{j,l,b}$ and the parachor, P_j are corrected by a factor of $8 \times 10^3 \eta_j$.

If the solute is water, both the liquid volume at normal boiling point, $V_{i,l,b}$ and parachor, P_i for solute are corrected by a factor 2. This factor also applies if it is detected from the SMILES formula that the species is an organic acid (a carboxyl group is found), except in the cases where the solvent is water, methanol or n-butanol.

Siddiqi–Lucas

Siddiqi and Lucas (Ref. 67) suggested correlations for liquid diffusion coefficients at infinite dilution for aqueous system (including gases) and for organic solutions. For normal paraffins systems, they recommended the Hayduk–Minhas model.

For aqueous solutions:

$$D_{i,j}^0 = 1.295436901 \times 10^{-17} \frac{T}{\eta_j^{1.026} (V_{i,l,b}^{0.5473})} \tag{2-245}$$

For all other systems, the equation for organic solution is used as:

$$D_{i,j}^0 = 1.459473761 \times 10^{-15} \frac{T(V_{j,l,b}^{0.265})}{\eta_j^{0.907}(V_{i,l,b}^{0.45})} \qquad (2\text{-}246)$$

Where T is the temperature, $V_{i,l,b}$ is the liquid volume at normal boiling point and η_j is the viscosity of the solvent.

Erkey–Rodden–Akgerman

The correlation by Erkey and others (Ref. 68) for liquid diffusion coefficients at infinite dilution in normal paraffins is:

$$D_{i,j}^0 = 94.5 \times 10^{-9} \frac{\sqrt{T}(V - V_j^{ref}) \times 10^6}{M_i^{0.239} M_j^{0.781} (\sigma_i \sigma_j \times 10^{-20})^{1.134}} \qquad (2\text{-}247)$$

where the reference volume is

$$V_j^{ref} = \frac{1}{\sqrt{2}} b_j N_{Av} \sigma_j^3 \qquad (2\text{-}248)$$

N_{Av} is Avogadro's number, and the deviation from closest packing volume is given by

$$b_j = 1.206 + 0.0632 \left(\frac{\sigma_i}{\sigma_j}\right) \qquad (2\text{-}249)$$

The correlation is fitted to normal paraffins, hydrogen, carbon monoxide and carbon dioxide diffusing in normal paraffins. The molecular weight M_i should be available for both solute and solvent. The Lennard–Jones diameter, σ_i is estimated from Bondi group contribution method (Ref. 69), and for some species are taken from Ref. 68 and Ref. 70 as:

TABLE 2-10: MOLECULAR DIAMETERS FOR SPECIES

SPECIES	$\sigma \times 10^{10}$ (M)
H_2	2.92
CO	3.72
CO_2	3.97
n-C_jH_{2j+2}	$(21.82 + 32.44 * j)^{1/3}$

To prevent the diffusion coefficients from becoming negative, the minimum difference of $(V - V_j^{ref})$ is considered to be 10^{-12} mol/m^3.

Liquid Phase Maxwell–Stefan Diffusivity

The Maxwell–Stefan liquid diffusion coefficients are calculated from the liquid diffusion coefficients at infinite dilution. The diagonal values should be ignored and are set to zero. The Vignes (Ref. 71) model for diffusion in binary solutions can be extended to multi-component systems (Ref. 72):

$$\text{Ð}_{i,j} = \prod_{k=1}^{n} (\text{Ð}_{i,j,\,x_k \to 1})^{x_k} \tag{2-250}$$

where $\text{Ð}_{i,j,\,x_k \to 1}$ denotes the Maxwell–Stefan liquid diffusion coefficient for species i and j in the limited of pure species k. If $k = j$, it represents a binary system of species i and j where i is infinitely diluted. In addition, at infinite dilution the thermodynamics factor (activity) (Ref. 57) becomes unity and the Maxwell–Stefan diffusivity equals to Fick diffusivity:

$$\text{Ð}_{i,j,\,x_j \to 1} = \text{Ð}_{i,j}^{0} = D_{i,j}^{0} \tag{2-251}$$

Similarly,

$$\text{Ð}_{i,j,\,x_i \to 1} = \text{Ð}_{j,i}^{0} = D_{j,i}^{0} \tag{2-252}$$

Models for the $\text{Ð}_{i,j,\,x_k \to 1}$ for $k \neq i$ and $k \neq j$ remain to be defined in such a way that symmetry is ensured:

$$\text{Ð}_{i,j} = \text{Ð}_{j,i} \tag{2-253}$$

and to ensure continuity if both species i and j vanish:

$$\lim_{x_i \to 0} \text{Ð}_{i,j,\,x_k \to 1} = \lim_{x_j \to 0} \text{Ð}_{i,j,\,x_k \to 1} \tag{2-254}$$

For binary systems, Equation 2-250 reduces to the Vignes interpolation formula.

Wesselingh–Krishna

Wesselingh and Krishna (Ref. 72) proposed:

$$\text{Ð}_{i,j,\,x_k \to 1} = \sqrt{D_{i,j}^{0} D_{j,i}^{0}} \tag{2-255}$$

leading to:

$$\mathcal{D}_{i,j} = (D_{i,j}^0)^{(1+x_j-x_i)/2}(D_{j,i}^0)^{(1+x_i-x_j)/2} \tag{2-256}$$

Kooijman–Taylor

Kooijman and Taylor (Ref. 73) found on a limited number of systems that this provides better results:

$$\mathcal{D}_{i,j,\,x_k\to1} = \sqrt{D_{i,k}^0 D_{j,k}^0} \qquad (k \neq i, j) \tag{2-257}$$

leading to:

$$\mathcal{D}_{i,j} = (D_{i,j}^0)^{x_j}(D_{j,i}^0)^{x_i} \prod_{\substack{k\,=\,1 \\ k\neq i,j}}^{n} (\sqrt{D_{i,k}^0 D_{j,k}^0})^{x_k} \tag{2-258}$$

Wesselingh and Bollen (Ref. 74) asserted that this is a reasonable estimate.

Krishna–van Baten

Krishna and van Baten (Ref. 75), on the basis of data obtained from molecular dynamic simulations, proposed the following Vignes-based (Ref. 71) interpolation:

$$\mathcal{D}_{i,j,\,x_k\to1} = (D_{i,k}^0)^{\left(\frac{x_i}{x_i+x_j}\right)}(D_{j,k}^0)^{\left(\frac{x_j}{x_i+x_j}\right)} \qquad (k \neq i, j) \tag{2-259}$$

The model reduces to the Kooijman–Taylor model for $x_i = x_j$. The value of $\mathcal{D}_{i,j,\,x_k\to1}$ is undefined in the limit of both $x_i \to 0$ and $x_j \to 0$. From a physical point of view this is inconsequential as the value cancels out in the expressions obtained for the fluxes using the Maxwell–Stefan equations. Nevertheless, in order to obtain well-defined values and composition derivatives of $\mathcal{D}_{i,j,\,x_k\to1}$ itself, the equation is modified to:

$$\mathcal{D}_{i,j,\,x_k\to1} = (D_{i,k}^0)^{\left(\frac{x_i+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)}(D_{j,k}^0)^{\left(\frac{x_j+\varepsilon_x}{x_i+x_j+2\varepsilon_x}\right)} \qquad (k \neq i, j) \tag{2-260}$$

where $\varepsilon_x = 10^{-10}$ is taken as a small composition. The limiting case for both $x_i \to 0$ and $x_j \to 0$ also reduces to the Kooijman–Taylor model. This equation leads to:

$$\mathcal{D}_{i,j} = (D_{i,j}^0)^{x_j}(D_{j,i}^0)^{x_i} \prod_{\substack{k=1 \\ k \neq i,j}}^{n} \left((D_{i,k}^0)^{\left(\frac{x_i + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)} (D_{j,k}^0)^{\left(\frac{x_j + \varepsilon_x}{x_i + x_j + 2\varepsilon_x}\right)} \right)^{x_k} \tag{2-261}$$

Surface Tension

Below the available surface tension models are presented.

GAS-LIQUID SURFACE TENSION

Ideal
The gas-liquid surface tension is predicted by ideally mixing the pure species correlations. It is independent of pressure, vapor temperature or composition.

$$\sigma_{vl} = \sum_i x_{i,l}\sigma_{i,vl} \tag{2-262}$$

where the vapor-liquid surface tension correlations, $\sigma_{i,vl}$, must be specified for all species i, and are evaluated at the temperature of the liquid phase.

Winterfeld
Following Winterfeld (Ref. 76), the vapor-liquid surface tension is predicted by mixing the pure species correlations according to

$$\sigma_{vl} = \frac{\displaystyle\sum_i \sum_j \frac{x_{i,l}x_{j,l}\sqrt{\sigma_{i,vl}\sigma_{j,vl}}}{\rho_{i,l}\rho_{j,l}}}{\left(\displaystyle\sum_i \frac{x_{i,l}}{\rho_{i,l}}\right)^2} \tag{2-263}$$

It is independent of pressure, vapor temperature and composition. The vapor-liquid surface tension correlations and liquid density correlations must be specified for all species i, and are evaluated at the temperature of the liquid phase.

References

1. A. Akerberg, *CFD analyses of the gas flow inside the vessel of a hot isostatic press*, Master of Science Thesis, KTH School of Industrial Engineering and Management, Stockholm, Sweden, 2012.

2. M.A. Trebble and P.R. Bishnoi, "Accuracy and consistency comparisons of ten cubic equations of state for polar and non-polar compounds", *Fluid Phase Equilibria*, vol. 29, pp. 465–474, 1986.

3. B.E. Poling, J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, McGraw-Hill, international edition, 2007.

4. M.C. Clapeyron, "Mémoire sur la puissance motrice de la chaleur," *Journal de l'École polytechnique*, vol. 23, pp. 153–190, 1834 (in French).

5. D.Y. Peng and D. Robinson, "A new two-constant equation of state," *Industrial and Engineering Chemistry: Fundamentals*, vol. 15, pp. 59–64, 1976.

6. C.H. Twu, J.E. Coon, and J.R. Cunningham, "A new generalized alpha function for a cubic equation of state, Part 1, Peng–Robinson equation," *Fluid Phase Equilibria*, vol. 105, pp. 49–59, 1995.

7. O. Redlich and J.N.S. Kwong, "On the thermodynamics of solutions an equation of state, fugacities of gaseous solutions," *Chemical Reviews*, vol. 44, no. 1, pp. 233–244, 1949.

8. G. Soave, "Equilibrium constants from a modified Redlich–Kwong equation of state," *Chemical Engineering Science*, vol. 27, no. 6, pp. 1197–1203, 1972.

9. M.S. Graboski and T.E. Daubert, "A modified Soave equation of state for phase equilibrium calculations, 3, systems containing hydrogen," *Industrial & Engineering Chemistry Process Design and Development*, vol. 18, no. 2, pp. 300–306, 1979.

10. J. R. Cooper, "Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam", *The International Association for the Properties of Water and Steam*, IAPWS R7-97, 2012.

11. K. Watanabe, "Revised Supplementary Release on Backward Equations for the Functions T(p,h), v(p,h) and T(p,s), v(p,s) for Region 3 of the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam," *The International Association for the Properties of Water and Steam*, Kyoto, Japan, Sep. 2004.

12. F. Marsik, "Supplementary Release on Backward Equations for Specific Volume as a Function of Pressure and Temperature v(p,T) for Region 3 of the IAPWS Industrial Formulation 1997 for the Thermodynamics Properties of Water and Steam," *The International Association for the Properties of Water and Steam*, Santorini, Greece, July 2005.

13. K.C. Chao and J.D. Seader, "A general correlation of vapor-liquid equilibria in hydrocarbon mixtures," *AIChE Journal*, vol. 7, no. 4, pp. 598–605, 1961.

14. J.H. Hildebrand and R.L. Scott, "The solubility of non-electrolytes," *Journal of Physical Chemistry*, vol. 55, no. 4, pp. 619–620, 1951.

15. H.G. Grayson and C.W. Streed, "Vapor-liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems," *6th World Petroleum Congress*, 19–26 June, Frankfurt am Main, Germany, IV, pp. 169–180, 1963.

16. J.H. Hildebrand, J.M. Prausnitz, and R.L. Scott. *Regular and Related Solutions*, Van Nostrand Reinhold Co., 1970.

17. G.M. Wilson, "Vapor-liquid equilibrium. xi. a new expression for the excess free energy of mixing," *Journal of the American Chemical Society*, vol. 86, pp. 127–130, 1964.

18. H. Renon and J.M. Prausnitz, "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE Journal*, vol. 14, no. 1, pp. 135–144, 1968.

19. D.S. Abrams and J.M. Prausnitz, "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems," *AIChE Journal*, vol. 21, no. 1, pp. 116–128, 1975.

20. A. Fredenslund, R.L. Jones, and J.M. Prausnitz, "Group-contribution estimation of activity coefficients in nonideal liquid mixtures," *AIChE Journal*, vol. 21, no. 6, pp. 1086–1099, 1975.

21. S. Skjold-Joergensen, B. Kolbe, J. Gmehling, and P. Rasmussen, "Vapor-liquid equilibria by unifac group contribution. revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 18, no. 4, pp. 714–722, 1979.

22. J. Gmehling, P. Rasmussen, and A. Fredenslund, "Vapor-liquid equilibria by unifac group contribution. revision and extension. 2," *Industrial & Engineering Chemistry Process Design and Development,* vol. 21, no. 1, pp. 118–127, 1982.

23. E.A. Macedo, U. Weidlich, J. Gmehling, and P. Rasmussen, "Vapor-liquid equilibria by unifac group contribution. 3. Revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 22, no. 4, pp. 676–678, 1983.

24. D. Tiegs, J. Gmehling, P. Rasmussen P, and A. Fredenslund, "Vapor-liquid equilibria by unifac group contribution. 4. Revision and extension," *Industrial &*

Engineering Chemistry Process Design and Development, vol. 26, no. 1, pp. 159–161, 1987.

25. H.K. Hansen, P. Rasmussen, A. Fredenslund, M. Schiller, and J. Gmehling, "Vapor-liquid equilibria by unifac group contribution. 5. Revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 30, no. 10, pp. 2352–2355, 1991.

26. R. Wittig, J. Lohmann, and J. Gmehling, "Vapor-liquid equilibria by unifac group contribution. 6. Revision and extension," *Industrial & Engineering Chemistry Process Design and Development*, vol. 42, no. 1, pp. 183–188, 2003.

27. K. Balslev and J. Abildskov, "Unifac parameters for four new groups," *Industrial & Engineering Chemistry Research*, vol. 41, pp. 2047–2057, 2002.

28. R.W. Hankinson and G.H. Thomson, "A new correlation for saturated densities of liquid and their mixtures," *AIChE Journal*, vol. 25, no. 4, pp. 653–663, 1979.

29. H.G. Rackett, "Equation of state for saturated liquids," *Journal of Chemical and Engineering Data*, vol. 15, no. 4, pp. 514–517, 1970.

30. L.I. Stiel and G. Thodos, "The thermal conductivity of nonpolar substances in the dense gaseous and liquid regions," *AIChE Journal*, vol. 10, no. 1, pp. 26–30, 1964.

31. M. Yorizane, S. Yoshimura, H. Masuoka, and H. Yoshida, "Thermal conductivities of binary gas mixtures at high pressures: nitrogen-oxygen, nitrogen-argon, carbon dioxide-argon, and carbon dioxide-methane," *Industrial & Engineering Chemistry Fundamentals*, vol. 22, no. 4, pp. 458–463, 1983.

32. A.L. Lindsay and L.A. Bromley, "Thermal conductivity of gas mixtures," *Industrial and Engineering Chemistry*, vol. 42, no. 8, pp. 1508–1511, 1950.

33. A. Wassiljewa, "Heat conduction in gas mixtures," *Physikalische Zeitschrift*, vol. 5, no. 22, pp. 737–742, 1904.

34. J.R. Cooper, "Release on the IAPS Formulation 1985 for the Thermal Conductivity of Ordinary Water Substance," *The International Association for the Properties of Water and Steam*, Berlin, Germany, Sep. 2008.

35. C.R. Wilke, "A viscosity equation for gas mixtures," *The Journal of Chemical Physics*, vol. 18, no. 4, pp. 517–520, 1950.

36. R.S. Brokaw, "Approximate formulas for the viscosity and thermal conductivity of gas mixtures. ii," *The Journal of Chemical Physics*, vol. 42, no. 4, pp. 1140–1147, 1965.

37. J.E. Lennard–Jones, "On the determination of molecular fields 1. from the variation of the viscosity of a gas with temperature," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, vol. 106, pp. 441–462, 1924.

38. W.H. Stockmayer, "Second virial coefficients of polar gases," *The Journal of Chemical Physics*, vol. 9, pp. 398–402, 1941.

39. F.M. Mourits and F.H.A. Rummens, "A critical evaluation of Lennard–Jones and Stockmayer potential parameters and of some correlation methods," *Canadian Journal of Chemical Engineering*, vol. 55, pp. 3007–3020, 1977.

40. T.A. Davidson, "A Simple and Accurate Method for Calculating Viscosity of Gaseous Mixtures", *Report of Investigations 9456*, United States Department of the Interior, Bureau of Mines, 1993.

41. J.A. Jossi, L.I. Stiel, and G. Thodos, "The viscosity of pure substances in the dense gaseous and liquid phases," *AIChE Journal*, vol. 8, no. 1, pp. 59–63, 1962.

42. K.S. Pedersen and P.L. Christensen, "Phase Behavior of Petroleum Reservoir Fluids," *CRC Press/Taylor & Francis Group*, 2007.

43. K.S. Pedersen, A. Fredenslund, P.L. Christensen, and P. Thomassen, "Viscosity of crude oils," *Chemical Engineering Science*, vol. 39, no. 6, pp. 1011–1016, 1984.

44. H.J.M. Hanley, W.M. Haynes, and R.D. McCarty, "The viscosity and thermal conductivity coefficients for dense gaseous and liquid methane," *Journal of Physical Chemistry*, vol. 6, no. 2, pp. 597–609, 1977.

45. K.S. Pedersen and A. Fredenslund, "An improved corresponding states model for the prediction of oil and gas viscosities and thermal conductivities," *Chemical Engineering Science*, vol. 42, no. 1, pp. 182–186, 1987.

46. R.D. McCarty, "A modified Benedict-Webb-Rubin equation of state for methane using recent experimental data," *Cryogenics*, pp. 276–280, May 1974.

47. S. Murad and K.E. Gubbins, "Corresponding states correlation for thermal conductivity of dense fluids," *Chemical Engineering Science*, vol. 32, no. 5, pp. 499–505, 1977.

48. J.R. Cooper, "Revised Release on the IAPWS Formulation 2008 for the Viscosity of Ordinary Water Substance", *The International Association for the Properties of Water and Steam*, Berlin, Germany, Sep. 2008.

49. K. Daucik, "Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance", *The International Association for the Properties of Water and Steam*, Plzen, Czech Republic, Sep. 2011.

50. J. Gabitto and M. Barrufet, "Experimental and theoretical determination of heavy oil viscosity under reservoir conditions," *Technical reports*, Office of Fossil Energy, USDOE Office of Fossil Energy, United States, 2002.

51. A. Missenard, "Conductivité thermique des liquides organiques d'une serie ou d'un 'groupe de liquides'," *Revue Générale de Thermique*, vol. 101, no. 5, pp. 649–660, 1970 (in French).

52. R.L. Rowley, G.L. White, and M. Chiu, "Ternary liquid mixture thermal conductivities," *Chemical Engineering Science*, vol. 43, no. 2, pp. 361–371, 1988.

53. R.L. Rowley, "A local composition model for multicomponent liquid mixture thermal conductivities," *Chemical Engineering Science*, vol. 37, no. 6, pp. 897–904, 1982.

54. W.D. Niven, "The Scientific Papers of James Clerk Maxwell", *Cambridge University Press*, 1890.

55. J.C. Maxwell, "On the dynamical theory of gases," *Philosophical Transactions of the Royal Society of London*, vol. 157, pp. 49–88, 1867.

56. J. Stefan, "Uber das Gleichgewicht und die Bewegung, insbesondere die Diffusion von Gasgemengen," *Sitzungsbrichte der Kaiserlichen Akademie der Wissenschaften Wien, 2te Abteilung a*, vol. 63, pp. 63–124, 1871.

57. R. Taylor and R. Krishna, "Multicomponent Mass Transfer," *Wiley-Interscience*, 1993.

58. E.N. Fuller, P.D. Schettler and J.C. Giddings, "A new method for prediction of binary gas-phase diffusion coefficients," *Industrial and Engineering Chemistry*, vol. 5, pp. 19–27, 1966.

59. E.N. Fuller, K. Ensley and J.C. Giddings, "Diffusion of halogenated hydrocarbons in helium. The effect of structure on collision cross sections," *The Journal of Physical Chemistry*, vol. 73, no. 11, pp. 3679–3685, 1969.

60. C.R. Wilke and C.Y. Lee, "Estimation of diffusion coefficients for gases and vapors," *Industrial and Engineering Chemistry*, vol. 47, no. 6, pp. 1253–1257, 1955.

61. P.D. Neufeld, A.R. Janzen, and R.A. Aziz, "Empirical equations to calculate 16 of the transport collision integrals $\Omega^{(l,s)*}$ for the Lennard–Jones (12-6) potential," *The Journal of Chemical Physics*, vol. 57, pp. 1100–1102, 1972.

62. C.R. Wilke and P. Chang, "Correlation of diffusion coefficients in dilute solutions," *AICHE Journal*, vol. 1, no. 2, pp. 264–270, 1972.

63. W. Hayduk and H. Laudie, "Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions," *AICHE Journal*, vol. 20, no. 3, pp. 611–615, 1974.

64. H.A. Kooijman, "A modification of the Stokes-Einstein equation for diffusivities in dilute binary mixture," *Industrial and Engineering Chemistry Research*, vol. 41, pp. 3326–3328, 2002.

65. M.T.Tyn and W.F Calus. Diffusion Coefficients in dilute binary mixtures. Journal of Chemical and Engineering Data, vol. 20, no. 1, pp. 106–109, 1975.

66. W.Hayduk and B.S.Minhas, "Correlation for prediction of molecular diffusivities in liquids," *Canadian Journal of Chemical Engineering*, vol. 60, no. 2, pp. 295–299, 1983.

67. M.A. Siddiqi and K. Lucas, "Correlations for prediction of diffusion in liquids", *The Canadian Journal of Chemical Engineering*, vol. 64, pp. 839–843, 1986.

68. C. Erkey, J.B. Rodden and A. Akgerman, "A correlation for predicting diffusion coefficients in alkanes", *The Canadian Journal of Chemical Engineering*, vol. 68, pp. 661–665, 1990.

69. A. Bondi, "van der Waals Volumes and Radii", *Journal of Physical Chemistry*, vol. 68, no. 3, pp. 441-451, 1964.

70. J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "The Molecular Theory of Gases and Liquids", *Wiley-Interscience*, 1964.

71. A. Vignes, "Diffusion in Binary Solutions," *Industrial and Engineering Chemistry Fundamentals*, vol. 5, pp. 189–199, 1966.

72. J.A. Wesselingh and R. Krishna, "Mass Transfer", *Ellis Horwood Ltd*, 1990, ISBN: 0-13-553165-9.

73. H.A. Kooijman and R. Taylor, "Estimation of diffusion coefficients in multicomponent liquid systems", *Industrial and Engineering Chemistry Research*, vol. 30, pp. 1217–1222, 1991.

74. J.A. Wesselingh and A.M. Bollen, "Multicomponent diffusivities from the free volume theory", *Chemical Engineering Research and Design*, 75(6):590–602, 1997.

75. R. Krishna and J.M. van Baten, "The Darken relation for multicomponent diffusion in liquid mixtures of linear alkanes: An investigation using molecular dynamics (MD) simulations," *Industrial and Engineering Chemistry Research*, vol. 44, pp. 6939–6947, 2005.

76. P.H. Winterfeld, L.E. Scriven, and H.T. Davis, "An approximate theory of interfacial tension of multicomponent systems: Applications binary liquid-vapor tensions," *AIChE Journal*, vol. 24, no. 6, pp. 1010–1014, 1978

77. E.C. Carlson, "Don't Gamble With Physical Properties For Simulation", *Chemical Engineering Progress*, vol. 92, no. 10, pp. 35–46, 1996.

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