CHEMCAD
PHYSICAL PROPERTIES

Version 5.6
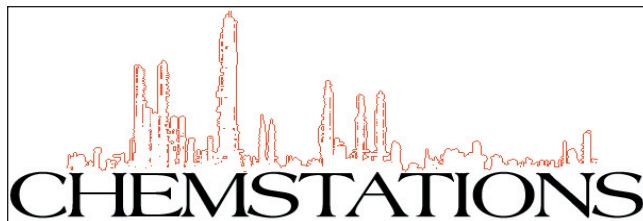User Guide
and Tutorial

CHEMICAL

PROCESS

SIMULATION

SOFTWARE

PHYSICAL PROPERTIES

Version 5.6

User's Guide

This manual uses the following abbreviations:

API	=	American Petroleum Institute
APISRK	=	The Soave-Redlich-Kwong equation-of-state as modified by the American Petroleum Institute.
BIPs	=	Binary interaction parameters
BREA	=	CHEMCAD batch reactor model
BWRS	=	Benedict-Webb-Rubin-Starling equation-of-state
CCB	=	CHEMCAD BATCH, the batch distillation module of CHEMCAD
CCDC	=	CHEMCAD DYNAMIC COLUMN, the dynamic column simulation module of CHEMCAD.
C_i	=	The adjustable external degree of freedom parameter for solvents in the UNIFAC for polymers K-Value method.
CCR	=	CHEMCAD ReACS, the batch reactor module of CHEMCAD
CCT	=	CHEMCAD THERM, the shell and tube rating module of CHEMCAD
C_w	=	Third parameter for HRNM Wilson
DE/k	=	SAFT distribution energy
DIPPR	=	Design Institute for Physical Properties Research
EOS	=	Equation-of-state
EREA	=	CHEMCAD equilibrium reactor model
ESD	=	Elliott-Suresh-Donahue equation-of-state
ESSO	=	ESSO (Exxon) method for predicting the vapor pressures of heavy hydrocarbon materials.
GIBS	=	CHEMCAD Gibbs free energy minimization reactor model
GS	=	Grayson-Stread K-Value method (basically an equation-of-state)
HRNM	=	Hiranama modification of the Wilson activity coefficient model
IG	=	Ideal gas
K	=	Watson-Nelson factor
K_i	=	Component K-Value
k_{ij}	=	Binary interaction parameters for EOS
KREA	=	CHEMCAD kinetic reactor model
LATE	=	Latent heat enthalpy model
LLE	=	Liquid-liquid equilibrium
m,n	=	MSRK parameters
MSRK	=	Modified Soave-Redlich-Kwong equation-of-state
P_c	=	Critical pressure
PIPE	=	Pipe segment unit operation
PPPD	=	Pool physical properties databank
P_r	=	Reduced pressure
PR	=	Peng-Robinson equation-of-state
PSRK	=	Predictive Soave-Redlich-Kwong equation of Gmehling
q	=	Surface parameter
r	=	Volume parameter
REAC	=	CHEMCAD stoichiometric reactor model
SAFT	=	Statistical Associating Fluid Theory equation-of-state
SCDS	=	Simultaneous Correction Distillation System. A rigorous model for distillation.
SFs	=	SAFT shape factor
SRK	=	Soave-Redlich-Kwong equation-of-state

T_b	=	Normal boiling temperature
Tc	=	Critical temperature
Tr	=	Reduced Temperature
TSRK	=	The extended Soave-Redlich-Kwong equation-of-state (developed by the US environmental protection agency for light gases dissolved in Methanol).
UPPD	=	Users physical properties databank
Vc	=	Critical volume
Vi	=	Liquid molar volume
VLE	=	Vapor-liquid equilibrium
VLLE	=	Vapor-liquid-liquid equilibrium
VP	=	Vapor pressure
Vs	=	SAFT characteristic volume
ΔHf	=	Heat of formation
ΔHr	=	Heat of reaction
ΔHv	=	Heat of vaporization
ΔP	=	Pressure drop
Ω, ω	=	Acentric factor
δ	=	Solubility parameter

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INTRODUCTION

The physical properties portion of CHEMCAD performs the following functions:

1. Provides data to represent the physical and transport properties for process simulations and related calculations. This data is contained in what we call the "Standard Physical Properties Databank. This database is stored in the CHEMCAD program file directory. The standard database contains data for approximately 2150 compounds (as of version 5.5). The user has access to view, but may not edit, the contents of the standard databank. Most of the data comes from the DIPPR databank.

2. Provides facilities for the user to create his/her own user component physical properties databank. This databank will contain physical and transport properties information supplied by the user and/or estimated by the program. This databank can be local to the user (called the "User component Databank)" or general to all company users (called the "Pool component Databank)."

3. Provides methods for the estimation of pure component properties based upon their molecular groups.

4. Provides methods for the estimation of grouped or "lumped" components based upon their average boiling point and specific gravity.

5. The creation of lumped or "psuedo-components" from True Boiling Point and/or ASTM Distillation Curves.

6. The creation of combustion solids from input weight percent of elements of the component.

7. Regression of pure component physical properties data.

8. File and data management facilities for editing and copying physical properties information.

9. Reporting and plotting facilities for documenting and reviewing physical properties information and data.

PHYSICAL PROPERTIES COMMANDS

This manual is concerned with the functions offered by the following commands:

i.   Under the Thermophysical Menu:

- The **Databank Command** with its subcommands:
  - ➢ View-Edit
  - ➢ New Component
  - ➢ Copy Component
  - ➢ Delete Component
  - ➢ BIP's
  - ➢ UNIFAC BIP's
  - ➢ Plot Properties
  - ➢ Neutral file import
  - ➢ List User Components

- The **Distillation Curves** Command

ii.   Under the Tools Menu:

- The Pure Regression Command

ACCESSING THE COMPONENT DATABANK

From the **Thermophysical** command on the main menu select **Databank**. This gives you access to the CHEMCAD component databank. From this menu, you can add new components to the user databank or edit properties for existing compounds. You may access components from the Chemstations provided databank, or user defined components. Please note that you cannot change any values in Chemstations databank directly. However, you are allowed to copy components from the Chemstations databank to the user's databank, and then edit these as a user-defined compound.

Following are the entries in the **Databank Menu** that apply to both the standard and the user databank. While you may view data for components numbered below 5000, you may not change values. You may edit user defined components, pool components, and pseudocomponents.

THE DATABANK MENU

ViewEdit Properties   Allows you to view the properties parameters of any component in the standard (Chemstations) databank and optionally change any parameter of user-defined components. You cannot edit properties for Chemstations' components (standard databank).

When you select the **View/Edit** command from the **Databank Menu**, the program will ask you to select a component from the database. Then the **View/Edit Component Data Menu** will appear.

The **View/Edit Component Data Menu** offers the following options:

Synonyms	Displays the standard component name and all available synonyms. For user-added components, CHEMCAD lets you enter as many synonyms as you need.
Formulas	Displays one or more structural formulas for standard compounds.
Minimum Required Data	Will display the minimum data required to use by equation of state method for K-Values and enthalpies. This is:

Molecular Weight	Acentric Factor
Critical Temperature	Specific gravity at 60°F
Critical Pressure	Polynomial ideal gas heat capacity coefficients.

Basic Data   Corresponds to the base set of properties found for the component

Molecular Weight	Acentric Factor
Critical Temperature	Melting Point

	Critical Pressure	Normal Boiling Point
	Critical Volume	Solubility Parameter
	Liquid Molar Volume	Dipole Moment
	IG Heat of Formation	
	IG Gibbs Energy of Formation	

Density Data

Equation coefficients of the DIPPR equations for the calculation of liquid density and solid density as a function of temperature.

Vapor Pressure and Heat of Vaporization Data

Equation coefficients oefficients of the DIPPR equations for the calculation of vapor pressure and heat of vaporization as a function of temperature.

Heat Capacity Data

Equation coefficients oefficients of the DIPPR equations for the calculation of ideal gas heat capacity, liquid heat capacity, and solid heat capacity as a function of temperature.

Viscosity Data

Equation coefficients oefficients of the DIPPR equations for the calculation of vapor viscosity and liquid viscosity as a function of temperature.

Thermal Conductivity and Surface Tension Data

Equation coefficients oefficients of the DIPPR equation for the calculation of vapor thermal conductivity, liquid thermal conductivity, and surface tension as a function of temperature.

UNIFAC Group Data

A tabulation of the UNIFAC groups for this molecule.

Other Data

All other non-electrolyte physical properties data is displayed under this option. This data includes:
Mean Average Boiling Point
Molecular Diameter
Heat of Vaporization
API Net Heating Value
API Gross Heating Value
    Liquid Volume Constant
    Modified Acentric Factor
    UNIQUAC Area and Volume Parameters
    WILSON Molar Volume
    Stiel Polar Factor
    Rackett Constant
    Polar Parameter
    Eps/K

	Watson K Factor
	API Gravity
	Specific Gravity at 60°F
	Antoine Vapor Pressure Parameters
	Two Parameters Equation Liquid Viscosity Parameters
	Two Parameters Equation Surface Tension
	MSRK Coefficients m and n
	Henry's Gas Law Constants
	ESD parameters

Electrolyte Data   Data used by the electrolytes thermodynamic system. This data includes:

- Electrolyte state
- Electrolyte type
- Molecular weight
- Electric charge
- Standard heat of formation
- Standard Gibbs free energy of formation
- Standard entropy
- Standard heat capacity

Classes   Shows the chemical group(s) or category(s) that the component belongs to.

Print Component Data Prints all the data which is available on a component.

Plot Component Data Plots the temperature dependent properties of a component.

CHEMCAD allows you to add up to 2000 components to the user databank. This permits you to save data for compounds that are not in the databank or if you wish to change individual properties for some of the standard components. Additional components can be added to the pool databank.

New Component   You can define new component properties for CHEMCAD in four ways. They can be estimated from a correlation suited for hydrocarbon pseudocomponents, estimated by one of two group contribution methods, estimated from input combustion solid data, or entered by the user from the keyboard. Please refer to the section entitled "Estimating Pure Component Physical Properties."

Copy Component   The copy command d allows you to choose a component to be copied to a new ID number. The component to be copied may be either a standard or user defined component. CHEMCAD will automatically assign the next free component ID number available to the new component.

Delete Component   This command erases a component from the list of user-defined components. When you select this option, the program will give you a list of the User-Added components in the library. It will not present you with all the components in the databank as you are not allowed to erase components from the Chemstations standard databank. You can identify the components by ID number, by formula, or by typing in its synonym (if available). It will then ask you to confirm the deletion.

Note: The program will deliberately leave a "gap" in the component numbering sequence when you delete one or more components on the databank. It will not pack the databank by moving higher numbered components to fill the gaps. This ensures that old jobs will always be compatible with database changes.

BIPs   This command allows you to view the binary interaction parameters currently stored in the CHEMCAD databank for any selected pair of components. This command is for viewing only, no editing is possible using this command.

UNIFAC BIPs   This command allows you to view the group data and information stored for the UNIFAC groups. The user cannot edit CHEMCAD groups or data, but may add and/or edit their own.

Plot Properties This command enables the user to plot the pure component properties of one or more components in any of the databanks. Properties can be plotted for more than one component at a time on the same graph. The procedure is:

Click on the Plot Properties command of the Databank Menu. The Component Selection dialog box will appear.

Select the component (s) to be plotted. Then click **OK**. The **Property Selection Menu** will appear.

Select the property to be plotted. The graph will be displayed .in a CHEMCAD plot window.

Neutral File Import   Allows data to be imported through the neutral file format, which is described elsewhere in this manual.

List User Components   Prepares a list of the names and ID numbers of all of the user added components. The results are displayed in **WORDPAD** for editing and printing.

THE DISTILLATION CURVE MENU

This option can be used to perform a petroleum assay analysis. A CHEMCAD simulation may contain up to 20 assays based on ASTM D86, ASTM D1160, D2887, or True Boiling Point (TBP) curves. The standard laboratory analysis records the temperature and amount distilled of an initial 100 cc of crude stock.

At least five points of a volume versus temperature curve are required. However, more points are strongly recommended. The program will extrapolate the 0 and 100% points if they are not entered. A maximum of 40 points may be specified. When a light-ends analysis is given, it overrides the 0% volume temperature.

The gravity of an assay must be specified. The minimum density information required is the bulk gravity. A gravity curve, mid-volume % versus gravity, may be entered. A gravity curve must have at least two points, but more are recommended; especially the curve endpoints. If you wish to enter both a gravity curve and a bulk gravity, the program will adjust the gravity curve to satisfy the bulk gravity condition.

If two or more streams are described by assays the user has the option of blending or not blending them. If blending is selected the Distillation Curve Characterization routine finds the temperature regions where the temperature versus volume curves overlap and calculates the average gravity of each cut in the

common temperature regions. Blending helps reduce the number of components in a flowsheet. The output of the Characterization consists of molar flow rates of the streams that are blended, which is sent to the flowsheet and key physical properties of each psuedocomponent, which is stored to the job subdirectory not in the physical properties databank.

PURE COMPONENT REGRESSION

The pure component regression package lets you fit equation parameters to experimental temperature dependent property data for pure components. As the databank stores equation parameters (not raw data) the regression package is extremely helpful. The regression package allows you to weight data to fit an area of the curve. Regression can be performed to obtain the following equation parameters from data:

Antoine Vapor Pressure
DIPPR Vapor Pressure
Heat of Vaporization
Liquid Density
Liquid Heat Capacity
Liquid Viscosity
Liquid Thermal Conductivity
Liquid Surface Tension
Polynomial Ideal Gas Heat Capacity
Vapor Viscosity
Vapor Thermal Conductivity
DIPPR Ideal Gas Heat Capacity

USING THE DATABANK

COMPONENT IDS

The ID number of a component indicates which databank stores the component. The standard databank components are read-only. User components may be changed by the user. Pool components may only be changed by a user who has management rights for the pool database.

Databank	ID Numbers
Standard	1-4999
Distillation Curve	5000-5999
Pool	6000-7999
User	8000-9999

LOCATION OF COMPONENT DATABASE FILES

The standard databank files are always stored in the CHEMCAD system directory. This is the location where CHEMCAD is installed.

By default, user added components are stored in the *work directory* for CHEMCAD. User added components may also be stored in the directory for the job that uses the components. The user added databank files have file extension .UF. There are typically 3 to 9 .uf files. The UF files do not represent individual components; they represent sets of property data.

If you create a new job, CHEMCAD will use the work directory user components for the new job. If you have a set of user components in a job folder, CHEMCAD will use these components with this job.

Distillation curve pseudocomponents will be stored in the local job folder with file extension .pcf.

Pool file databank (optional) are stored in the Pool Directory.

From the **File** menu in CHEMCAD, select **Misc Settings** to view (or change) the work directory location (or the pool file directory location).
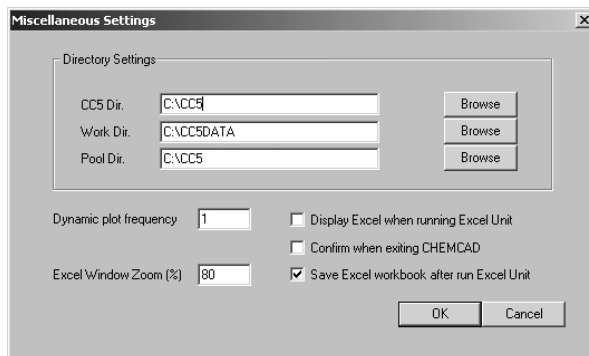
LOADING USER COMPONENTS FOR A SIMULATION

A simulation does not store data on the user added components. A simulation stores the component ID numbers used in the simulation. This distinction becomes important when you share work with another CHEMCAD user / computer.

CHEMCAD uses the following procedure to find user-added components for a simulation.

First – it will look in the current Job directory for a component with the same number. For example, if you open job c:\cc5data\phenol, CHEMCAD will look in this folder for a user defined databank.

Next – if the job directory doesn't contain user components, CHEMCAD will look in the work directory. (e.g., c:\cc5data).

SHARING USER COMPONENTS WHEN YOU SHARE A JOB

If you are sharing a job which uses user components, it is important to transfer both the job and the user components. If you transfer only the user components, your coworker will use their own user component

databank when they open your job. It is important to move a copy of your user databank into the job folder which you share with a coworker.

To simplify this process, CHEMCAD has a command to package the user components with the job folder for you. If you use the **File** menu command **Export Job**, CHEMCAD will copy the user component files into the exported job folder.

> Open CHEMCAD, but do not open a job.
>
> Go to the **File** menu and select **Export Job**.
>
> Select the job to export, and a destination for the exported copy.
>
> The exported copy will include your user component databank. Share the exported job folder with your colleague.

To perform these actions manually:

> Make a copy of the job folder.
>
> Copy the files gp*.uf from your work directory into the copied folder.
>
> Send the copied folder (with gp*.uf files) to your colleague.

PHYSICAL PROPERTIES AND THEIR DEFINITIONS

SOURCES OF DATA FOR CHEMCAD PROPERTIES

If you see a number entered for a component in the standard databank, it was entered by Chemstations staff. Chemstations only uses reliable sources for data. The primary source for the databank is the DIPPR databank. Secondary sources include peer reviewed published journals, texts, and vendor data.

PHYSICAL PROPERTIES STORED BY CHEMCAD

For any molecular (non-electrolyte) component in the CHEMCAD databank it is possible to store any or all of the following information:

1. **Pure Component Constant Properties**

   Properties given by a single value are called constant properties. CHEMCAD has the capability of storing the following pure component constant properties for any component.

   - Molecular Weight
   - Critical temperature
   - Critical pressure
   - Critical volume
   - Melting point
   - Normal boiling point
   - IG heat of formation
   - IG Gibbs free energy of formation
   - Acentric factor
   - Solubility parameter
   - Dipole moment

- Mean average boiling point
- Heat of vaporization at the NBP
- Liquid volume constant
- Molecular diameter
- Modified acentric factor
- UNIQUAC area parameter
- UNIQUAC volume parameter
- Wilson molar volume
- Stiehl polar factor
- Rackett constant
- Polar parameter
- Eps/K
- Watson factor
- API gravity
- Specific gravity 60°F

2. **Temperature Dependent Properties**

Equations are used to calculate temperature dependent properties in CHEMCAD. Equation coefficients are stored for the following properties:

- Vapor pressure (for both DIPPR and the Antoine equations)
- Heat of vaporization
- Ideal gas heat capacity (for both the DIPPR and the Polynomial equations)
- Liquid heat capacity
- Solid heat capacity
- Liquid density
- Solid density
- Vapor viscosity
- Liquid viscosity (for both the DIPPR and the two-term equations)
- Vapor thermal conductivity
- Liquid thermal conductivity
- Liquid surface tension (for both the DIPPR and the two-term equations)
- Henry's Constants
- Two parameter surface tension equation

3. **Parameters for vapor liquid equilibrium models**

CHEMCAD also stores values for the following:

- *n* and *m* parameters for the Modified SRK equation
- SAFT and ESD parameters
- UNIFAC subgroup assignments for the molecule.

4. **Attributions and other information**

In addition to the above properties, CHEMCAD stores the following information for each component:

- CASN – CAS registry number for the component

- Synonyms – up to six per component.
- Formula – both molecular and structural formulas can be stored.
- Class – an attribute defining which chemical category a compound falls into (hydrocarbon, ester, alcohol, (etc.). These classes are primarily for user classification.

5. **Calculated Properties**

   The following properties are calculated by CHEMCAD. These are constant properties of a mixture, and generally apply to petroleum mixtures.

   - API net heating value
   - API gross heating value
   - Flash point
   - Pour point
   - Aniline point
   - Smoke point
   - Freeze point
   - Cloud point
   - Cetane index
   - Refractive index

It is not necessary for a component to have a value for all the properties listed above. No component in the database has a value for every property. Where possible, each component has sufficient values to be used in its normal applications.   Absent properties are often estimated by CHEMCAD, either automatically or at the user's request.

PROPERTY DEFINITIONS AND CONVENTIONS

Pure component properties in CHEMCAD are defined below. Information relevant to use in CHEMCAD is also given.

Pure Component Constant Properties

MOLECULAR WEIGHT

All molecular weights have been calculated on the basis of the atomic weights of the elements as given in IUPAC, "Atomic Weights of the Elements 1989," Pure App. Chem. 63, 975 (1991).

THE CRITICAL PROPERTIES: T_C, P_C, AND V_C

The critical point is the set of physical conditions at which the physical properties of the liquid and gas become identical. The critical temperature, Tc, critical pressure, Pc, and the critical volume, Vc, define the physical conditions of the critical point.

MELTING POINT

The **melting point** is the temperature at which melting occurs under 101325 Pa (1 atmosphere). CHEMCAD does not directly use the melting point for calculations. The melting point is stored because it

is useful information, and can be accessed by user unit operations. An example job demonstrates the use of melting point in a user added unit operation.

THE NORMAL BOILING POINT

The normal boiling point is the temperature at which the vapor pressure equals 101325 Pa (1 atmosphere).

THE ENTHALPY (HEAT) OF FORMATION

The enthalpy (heat) of formation of an ideal gas is the increment in enthalpy associated with the reaction of forming the given compound in a [theoretical] ideal gas state from the elements in their standard state defined as the existing phase at a temperature of 298.15 K and a pressure of 101325 Pa.

THE GIBBS ENERGY OF FORMATION

The Gibbs energy of formation of an ideal gas is the increment in Gibbs free energy associated with the reaction of forming the given compound in its [theoretical] ideal gas state from the elements in their standard state defined as the existing phase at a temperature of 298.15 K and a pressure of 101325 Pa.

THE ACENTRIC FACTOR

The acentric factor, ω, is a parameter which helps to specify the VP curve which in turn correlates the rest of the thermodynamic variables.

As originally proposed, ω represents the acentricity or non-sphericity of a molecule force field. For monatomic gases ω is therefore essentially zero. For methane it is still very small. However, for higher-molecular-weight hydrocarbons, ω increases. It also rises with polarity. At present, ω is very widely used as a parameter which in some manner is supposed to measure the complexity of a molecule with respect to both the geometry and polarity. The large values of ω for some polar compounds ($\omega > 0.4$) are not meaningful in the context of the original meaning of this property. Deviations from simple fluid behavior are evident when $\omega > 0$.

The classic definition of acentric factor (other calculation methods exist) is:

$$\omega = -1 - \log\left(\frac{P^{sat}}{P_c}\right) \qquad T_r = 0.7$$

Note: The specification of T_c, P_c and ω provides two points on the VP curve. T_c and P_c specify the terminal point of the VP curve. ω specifies VP at $T_r = 0.7$.

SOLUBILITY PARAMETER

A cause of non-ideality common to all solutions results from differences in the van der Waals forces of attraction among the different species present. Hildebrand has expressed this force in terms of a solubility parameter. For liquid solutions the solubility parameter of a particular component present is expressed in terms of internal energy of vaporization of the pure component saturated at the temperature of interest divided by its molar volume in the saturated liquid state. The internal energy of vaporization includes expansion to its ideal gaseous state.

The solubility parameter, δ_l, is defined as the square root of the cohesive energy density. The cohesive energy density is the amount of energy per unit volume that keeps the fluid in the liquid state. An excellent approximation for the cohesive energy of a component is the heat of vaporization, which is the amount of energy that must be supplied to vaporize the fluid. The solubility parameter is calculated from:

$$\delta_i = \left[\frac{\Delta H_V}{v}\right]^{\frac{1}{2}} = \left[\Delta H_V / RT\rho\right]^{\frac{1}{2}}$$

where ΔH_v =   heat of vaporization
        T   =   temperature
        R   =   ideal gas constant
        ρ =   liquid molar density
        V   =   molar volume

It is calculated from the heat of vaporization and liquid density values obtained from the correlation equations for these properties. The value is given at 298.15 K and 101325 Pa when the substance is a liquid at this temperature and pressure. If the substance is a solid at 298.15 K the value is calculated at its triple point. If the substance is a gas at 298.15 K the value is calculated at its normal boiling point.

DIPOLE MOMENT

About one hundred years ago it was noticed that some liquids have a small dielectric constant that is nearly independent of the temperature and that others have a larger value that decreases rapidly with increase in the temperature. It was postulated that liquids of the first category, called nonpolar liquids, consist of molecules with no electric dipole moment, and that the liquids of the second category, called polar liquids, consist of molecules that have a dipole moment.

A molecule has an electric dipole moment if its center of positive charge does not coincide with its center of negative charge. The magnitude of the dipole moment for two charges $+q$ and $-q$ the distance, d ,apart is qd. The molecular dipole moment can be estimated by vector addition of individual bond moments if the bond angles are known.

MEAN AVERAGE BOILING POINT

For complex mixtures such as petroleum fractions, it is impractical to analyze the entire mixture to define the concentration of all the components. These undefined mixtures are usually characterized by parameters that are derived from normal inspection tests, such as an ASTM D86 or D1160 distillation curve, and the specific gravity of the mixture. Many characterizing parameters have been proposed, but very few are generally useful.

Among the useful parameters are four different boiling points and the Watson characterization factor, K. Each boiling point reduces to the normal boiling point for pure hydrocarbons and is significant for a different group of correlations. These four quantities are defined by the following equations.

Volumetric average boiling point:

$$VABP = \sum_{i=1}^{n} x_{vi} T_{b_i}$$

where x_{vi} =   volume fraction of component i

T_{b_i} = normal boiling point of component i. Either Fahrenheit or Rankine units may be used for volumetric average boiling point

Molal average boiling point:

$$MABP = \sum_{i=1}^{n} x_i T_{b_i}$$

Weight average boiling point (WABP):

$$WABP = \sum_{i=1}^{n} x_{wi} T_{b_i}$$

where x_{wi} = weight fraction of component i

Cubic Average Boiling Point (CABP):

$$CABP = \left(\sum_{i=1}^{n} x_{vi} T_{b_i}^{1/3} \right)^3$$

Mean average boiling point (MeABP):

$$MeABP = \frac{MABP + CABP}{2}$$

HEAT OF VAPORIZATION AT THE NORMAL BOILING POINT, ΔH_v

When heat is added to a pure component liquid at its boiling point, the temperature does not change. Instead a certain amount of liquid becomes a gas. The heat absorbed on vaporization at the boiling point is the heat of vaporization. The value stored in this field is the heat of vaporization at the normal boiling point, i.e., at atmospheric pressure.

Since CHEMCAD also stores coefficients for the temperature dependent DIPPR heat of vaporization equation, the ΔH_v stored here is never used by CHEMCAD unless the DIPPR coefficients are absent.

The heat of vaporization decreases with temperature and is zero at the critical point. Therefore, if the DIPPR coefficients are missing and the heat of vaporization at the NBP is used in the heat balance, the following equation is used to account for temperature dependence:

$$\Delta H_{v_2} = \Delta H_{v_1} \left(\frac{1 - T_{r_2}}{1 - T_{r_1}} \right)^{0.38}$$

where ΔH_v = heat of vaporization
            T_r = reduced temperature

LIQUID VOLUME CONSTANT

The liquid volume constant is an empirical parameter used in the calculation of liquid density:

$$\text{Liquid volume} = \text{Volume Constant } (5.7 + 3T_r)$$

where   Volume Constant   =   the liquid volume constant cc/gmole
          T_r =   reduced temperature

MOLECULAR DIAMETER

This is the physical diameter of the molecule in Angstroms. It is used to calculate vapor viscosity when the DIPPR data is absent.

MODIFIED ACENTRIC FACTOR

This is a modification of the acentric factor described above. It is used only by the MSRK equation of state as described in:

"Compilation of Parameters for a Polar Fluid Soave-Redlich-Kwag Equation of State"; Jamal A. Sandarusi, Arthur J. Kidney, and Victor F. Yesavage; Ind. Eng. Chem. Proc. Des. Dev.; 1988, 25, 957-963.

UNIQUAC SURFACE AREA AND VOLUME PARAMETERS

Both the UNIFAC and UNIQUAC activity coefficient equations require surface area and volume parameters for each molecule in the mixture in order to calculate the combinatorial contribution term. The UNIFAC equation estimates these parameters by summing the area and volume parameters of the functional groups in the molecule. However, for the UNIQUAC equation, CHEMCAD stores and uses unique, molecule specific area and volume parameters if they are available. These parameters were taken from the DeChema Series and are stored in these fields. If these UNIQUAC area and volume parameters are not present, then CHEMCAD estimates them using the UNIFAC group contribution method.

Please note:

1. UNIQUAC area and volume parameters are used only by the UNIQUAC equation.

2. If the user wants to force UNIQUAC to use the UNIFAC area and volume parameters, he/she can do so by selecting the "UNIQUAC/UNIFAC" option on the K-Value dialogue box.

WILSON MOLAR VOLUME

This parameter is no longer used by CHEMCAD.

STIEL POLAR FACTOR, X

The Curl-Pitzer equation relates the reduced vapor pressure to the acentric factor in the following way:

$$\ln P_{vp_r} = f^{(0)}(T_r) + \omega f^{(1)}(T_r)$$

The functions $f^{(0)}$ and $f^{(1)}$ expressed in analytical form as follows:

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 \, T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 \, T_r^6$$

If this estimated reduced vapor pressure is called $P_{vp_r,normal}$, the Stiel polarity factor X is given as:

$$X \equiv \log \frac{P_{vp_r}}{P_{vp_r,normal}} \qquad \text{at } T_r = 0.6$$

If the material has a vapor pressure well correlated by the Curl-Pitzer equation, X will, of course, be zero. Polar materials have been shown to deviate from this Pitzer vapor-pressure correlation at low values of T_r (below $T_r \cong 0.60$). [Note that all must fit at $T_r = 0.7$ by the definition of the acentric factor.] The definition of X thus quantifies this deviation. This value is used to estimate the viscosity of polar compounds if both the DIPPR data and the two-parameter data are missing.

THE RACKETT CONSTANT, Z_{RA}

The Modified Rackett equation which was developed by Rackett and later modified by Spencer and Danner is used to estimate saturated liquid volumes.

$$V = \frac{RT_c}{P_c} \left(Z_{RA} \right) \left[1 + (1 - T_r) \right]^{2/7}$$

Where Z_{RA} is the Rackett Constant and is unique for each compound.

The Rackett method is only used to calculate liquid density if the user selects it or the DIPPR data is absent.

POLAR PARAMETER

The Polar Parameter, δ is defined as:

$$\delta = \frac{\mu_p^2}{2\varepsilon\sigma^3}$$

where μ_p = the dipole moment
σ = the molecular diameter
ε = the Stockmayer energy parameter

This value is used to calculate the viscosity of polar, gaseous compounds. It is only used if selected, or if the DIPPR data is missing.

EPS/K, ε/k

Let $\psi(r)$ be the intermolecular energy between two molecules separated by distance r. At large separation distances, $\psi(r)$ is negative; the molecules attract each other. At small distances, repulsion

occurs. The minimum in the ψ (r) –vs.-r curve, where the forces of attraction and repulsion balance, is termed the **characteristic energy ε**. For any potential curve, the dimensionless temperature T* is related to ε by:

$$T^* = \frac{kT}{\varepsilon}$$

where **k is Boltzmann's constant**.

THE WATSON FACTOR

The Watson characterization factor, *K*, is defined by the equation:

$$K = \frac{(MABP)^{\frac{1}{3}}}{Sp.Gr.}$$

where MABP = the mean average boiling point in degrees Rankine
Sp.Gr. = the specific gravity at 60°F

The Watson *K* is an approximate index of paraffinicity, with high values corresponding to high degrees of saturation. For identifiable hydrocarbon mixtures, the Watson *K* is given by the equation:

$$K = \sum_{i=1}^{n} x_{wi} K_i$$

where K_i is the Watson *K* for the component *i*.

API GRAVITY

The API Gravity is defined as:

$$API = \frac{141.5}{Sp.Gr.} - 131.5$$

where Sp.Gr. = specific gravity.

SPECIFIC GRAVITY AT 60°F

The specific gravity of compound *i* is defined as:

$$SG = \frac{\rho_i}{\rho_{H_2O}} \quad \bigg| \quad at\ 60°F.$$

Calculated Properties

API NET HEATING VALUE, ΔH$_C$

The net heat of combustion is the heat evolved in a combustion beginning and ending at 60°F with products of gaseous water and carbon dioxide. Therefore,

$$\Delta H_c = Q - c\lambda_{H_2O}$$

where   ΔH   =   net heat of combustion, in BTU'S per pound of fuel
         Q   =   gross heat of combustion, in BTU'S per pound of fuel
         c   =   pounds of water formed per pound of fuel consumed
         λ_{H_2O} =   heat of vaporization of water at 60°F and at its vapor pressure, in BTU'S per pound of fuel

API GROSS HEATING VALUE

The heat of combustion of a substance is the heat evolved when that substance is converted to its final oxidation products by means of molecular oxygen. The following reaction represents the complete combustion of a hydrocarbon:

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \rightarrow \frac{b}{2}H_2O + a(CO_2)$$
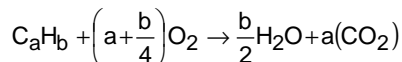
The standard heat of combustion is defined as the change in enthalpy resulting from the combustion of a substance, in the state that is normal at 77°F and atmospheric pressure, beginning and ending at a temperature of 77°F. The gross heat of combustion is the same as the standard heat of combustion except that the combustion begins and ends at 60°F rather than 77°F. The normal state for the water formed by the reaction is liquid in both cases.

The difference between the standard and the gross heats of combustion is the difference between the sensible heat changes of the products and the reactants from 60°F to 77°F. This sensible heat difference is usually negligible in comparison with the heats of combustion, so the gross and standard heats of combustion are approximately equal.

FLASH POINT

Flash point is the lowest temperature at which application of a test flame causes the vapor of the specimen to ignite at test conditions corrected to standard pressure.

In CHEMCAD the flash point of a material is calculated as follows:

$$FPT = \frac{1}{-0.014568 + (2.84947/T_{10}) + 0.001903 \log (T_{10})}$$

where   FPT   =   flash point temperature, °R
         T_{10} =   ASTM D86 10% temperature for the material. (Volume %, °R)

Note: The flash point temperature can be displayed in any temperature units, but CHEMCAD calculates internally in Rankine.

POUR POINT

Pour point is the lowest temperature at which petroleum fraction will flow or can be poured.

Within CHEMCAD the pour point temperature is calculated like so;

         A   =   0.61235 - 0.473575 ∗ TSG
         B   =   0.310331 - 0.32834 ∗ TSG

where   TSG   =   the total or overall specific gravity of the petroleum fraction. It is
                     calculated as shown;

$$TSG = \frac{wtotal}{0.0685295 * bps} = \frac{M_T * M}{0.0685295 * bps}$$

where   wtotal   =   total mass flowrate
         MT   =   total molar flowrate
         M   =   average molecular weight
         bps   =   standard barrels per day

The pour point is calculated as follows:

$$T_{PP} = 234.85\ S^{2.970566}\ M^{(0.61235 - 0.473575S)}\ \nu_{100}^{(0.310311 - 0.32834S)}$$

where   TPP   =   pour point of petroleum fraction, in degrees Rankine
         $\nu100$ =   kinematic viscosity at 100 F, in centistokes
         S   =   specific gravity at 60 F/ 60 F
         M   =   molecular weight of petroleum fraction

ANILINE POINT

Aniline point is the lowest temperature at which a petroleum fraction is completely miscible with an equal volume of aniline. ASTM Procedure D611 is used to determine the experimental aniline points.

In CHEMCAD the following equation is used to estimate the aniline point of a petroleum fraction.

$$AP = -1253.7 - 0.139\ MeABP + 107.8\ K + 868.7\ S$$

where   AP   =   aniline point of petroleum fraction, R
         MeABP   =   mean average boiling point, R
         S   =   specific gravity at 60 F/ 60 F
         K   =   Watson K factor

This equation reproduced experimental values of aniline point to within an average deviation of 4.2 R for 343 data points having a mean average boiling point less than 750 F. Including data with mean average boiling points greater than 750 F, the equation reproduced experimental values of aniline point within an average deviation of 4.7 R for 475 data points. The equation should be used with caution when estimating pure compound aniline points and petroleum fractions with a mean average boiling point greater than 750 degrees Fahrenheit.

SMOKE POINT

The smoke point is the height in millimeters of the flame that is produced in a lamp at standard conditions without causing smoking. ASTM Procedure D1322 is a standard method for experimental determination.

In CHEMCAD the smoke point is estimated as follows:

$$\ln SP = -1.028 + 0.474\ K - 0.00168\ MeABP$$

where   SP   =   Smoke point of petroleum fraction, mm

MeABP   =   mean average boiling point, R
K   =   Watson K factor

This equation was evaluated over the following smoke point, specific gravity, and mean average boiling point ranges.

	Range of Data
Smoke point, mm	15-33
Specific gravity, 60F/60F	0.7-0.86
Mean average boiling point, F	200-550

This equation is not recommended for the unlikely case of a fraction of low specific gravity (S<0.8) with a mean boiling point greater than 1000 F.

The equation reproduced experimental values of spoke point to within an average error of 6.3 percent.

FREEZE POINT

The freezing point of a petroleum fraction is the temperature at which solid crystals formed on cooling disappear as the temperature is raised. ASTM Procedure D2386 is a standard method for experimental determination.

The following equation is used to estimate the freezing point of petroleum fractions.

$$FRP = -2390.42 + 1826\ S + 122.49\ K - 0.135\ MeABP$$

where   FRP   =   Freezing point of petroleum fraction, R
        MeABP =   mean average boiling point, R
        K   =   Watson K factor
        S   =   specific gravity of petroleum fraction, 60F/60F

This equation was evaluated over the following ranges of freezing points, mean average boiling points and specific gravities.

	Range of Data
Freezing point, R	320-510
Specific gravity, 60F/60F	0.74-0.90
Mean average boiling point, R	725-1130

This equation may be reasonably extrapolated beyond these ranges.

The equation reproduced experimental values of freezing point to within 7.2 degrees Rankine.

CLOUD POINT

The cloud point of a petroleum product is the temperature at which its solid paraffin content, normally held in solution, begins to solidify and separate in tiny crystals, causing the oil to appear cloudy. Procedure ASTM D97 is used to determine experimental values of cloud point.

The following equation is used to estimate the cloud point of petroleum fractions.

$$\log CP = -7.41 + 5.49 \log MeABP - 0.712\, MeABP^{0.315} - 0.133\, S$$

where   CP   =   Cloud point of petroleum fraction, R.

MeABP   =   mean average boiling point, R.

S   =   specific gravity, 60F/60F.

This equation was evaluated with 834 points of experimental data over the following ranges of cloud point and mean average boiling point.

	Range of Data
Cloud point, R	375-560
Specific gravity, 60F/60F	0.77 to 0.93
Mean average boiling point, R	800 to 1225

The equation can be reasonably extrapolated beyond the tested data range.

The equation reproduced experimental values of cloud point to within 7.4 degrees Rankine.

CETANE INDEX

The cetane index is the number equal to the percentage of cetane in a blend of cetane and alpha methyl naphthalene having the same ignition quality as a sample of the petroleum fraction.

The following equation is used to calculate the cetane index of petroleum fractions.

$$CI = 415.26 - 7.673\, API + 0.186\, MeABP + 3.503\, API \log MeABP - 193.816 \log MeABP$$

where   CI   =   cetane index of petroleum fraction.

API   =   API gravity.

MeABP   =   mean average boiling point, F.

This equation was evaluated over the following ranges of API gravity and ASTM D86 mean average boiling points.

	Range of Data
API gravity	27-47
Mean average boiling point, F	360-700

The equation is not recommended for mean average boiling points < 250 F.

The equation reproduced values of cetane index to within an average error of 2.9 % for 150 data points.

REFRACTIVE INDEX

Light traversing a substance has a velocity different from light traversing a vacuum. The ratio of the velocity of light in a vacuum to that in a substance is the *index of refraction* of the substance. The interaction between the light and the substance that causes the index of refraction of the substance to differ from unity is the polarization of the atoms or molecules of the substance by the electric vector of the light.

The following equation is to be used to predict the refractive index of petroleum fractions.

$$n = \left[\frac{1 + 2I}{1 - I} \right]^{1/2}$$

Values of I are calculated from equation:

$$I = 2.266 \times 10^{-2} \exp\left(3.905 \times 10^{-4} \text{ MeABP} + 2.468 \text{ S} - 5.704 \times 10^{-4} \text{ MeABP S}\right) *$$

$$\text{MeABP}^{0.0572} \text{ S}^{-0.720}$$

where   n   =   refractive index at 68F
          I   =   modified Huang characterization parameter at 68F
        MeABP   =   mean average boiling point, D86, R
        S   =   specific gravity, 60F/60F

These equations were used to evaluate refractive index data for petroleum fractions with mean average boiling point, specific gravity, and refractive indices in the following ranges listed.

	Range of Data
Mean average boiling point, F	100-950
Specific gravity, 60F/60F	0.63-0.97
Refractive index at 68F	1.35-1.55

The method may also be used to predict the refractive index for pure hydrocarbons by using the normal boiling point in place of the mean average boiling point.

These equations reproduced experimental values for refractive index within an average absolute percent error of 0.3%.

TEMPERATURE DEPENDENT PROPERTIES

Temperature dependent properties such as vapor pressure, liquid density, etc., are represented by equations which fall into two different categories.

1. Equations in the DIPPR equation forms

2. Equations which are not in a DIPPR form

The program uses the DIPPR form unless;

1. The DIPPR coefficients are not present, or

2. The user specifically tells the program to do otherwise.

The DIPPR equations were developed to allow an accurate fit of a temperature dependent property with a single parameter set. The equations provide a better fit to data and better extrapolation beyond data then is obtained using a simple polynomial.

TEMPERATURE DEPENDENT PROPERTIES IN THE DIPPR FORM(S)

CHEMCAD can use DIPPR coefficients for the following temperature dependent properties:

1. Vapor pressure

2. Heat of Vaporization

3. Ideal gas heat capacity

4. Liquid heat capacity

5. Solid heat capacity

6. Vapor Viscosity

7. Liquid Viscosity

8. Vapor thermal conductivity

9. Liquid thermal conductivity

10. Liquid surface temperature

When the DIPPR coefficients are present for any property, the following specific information is provided:

- The engineering units of the property (SI units are always used for DIPPR equations)
- The DIPPR equation form number (see the equations, below)
- The "Low T"; i.e., the low temperature limit of the correlated data
- The "Low Value" which is the value of the property at the low temperature limit
- The "High T"; i.e., the high temperature limit of the correlated data
- The "High Value" which is the value of the property at the high temperature limit

The equation coefficients for calculating the property

THE DIPPR EQUATION FORM NUMBERS

The system of units for all DIPPR equations is SI; T is always in Kelvin and the coefficients must be compatible to the SI form of the equation. The following table lists the physical properties that can be modeled using these equations and the units they are calculated in:

Temperature-Dependent Property	Units
Solid density	(kmol/m3)
Liquid density	(kmol/m3)
Vapor pressure	(Pa)
Heat of vaporization	(J/kmol)
Solid heat capacity	(J/kmol-K)
Liquid heat capacity	(J/kmol-K)
Ideal gas heat capacity	(J/kmol-K)

Liquid viscosity   (Pa-sec)
Vapor viscosity   (Pa-sec)
Liquid thermal conductivity   (W/m-K)
Vapor thermal conductivity   (W/m-K)
Surface Tension   (N/m)

Each of the general-purpose DIPPR equations is listed below. It is not always necessary to specify all coefficients when using an equation; the number of coefficients that can be specified is noted for each equation.

Equation 100: $Y = A + BT + CT^2 + DT^3 + ET^4$

Any number of coefficients, from 1 to 5 may be specified.

Equation 101: $Y = \exp\left[A + \dfrac{B}{T} + C\ln(T) + DT^E\right]$

2, 3, or 5 coefficients may be specified.

Equation 102: $Y = AT^{\left[B/\left(1 + CT + DT^2\right)\right]}$

2, 3, or 4 coefficients may be specified.

Equation 103: $Y = A + B * \exp\left[\dfrac{-C}{T^D}\right]$

All 4 coefficients must be specified.

Equation 104: $Y = A + B/T + C/T^3 + D/T^8 + E/T^9$

2, 3, 4, or 5 coefficients may be specified.

Equation 105: $Y = \dfrac{A}{B^{\left[1 + (1 - T/C)\right]^D}}$

All 4 coefficients must be specified.

Equation 106: $Y = A * \left(1 - Tr\right)^{\left[B + CTr + DTr^2 + ETr^3\right]}$

Tr is the reduced temperature (T/ Tc).

2, 3, 4, or 5 coefficients may be specified and the critical temperature must be specified for this component.

Equation 107: $Y = A + B * \left[\dfrac{(C/T)}{\sinh(C/T)}\right]^2 + D\left[\dfrac{(E/T)}{\cosh(E/T)}\right]^2$

Either 3 or 5 coefficients must be specified.

Equation 114: $Y = \dfrac{A^2}{T_r} + B - 2ACT_r - ADT_r^2 - \dfrac{C^2 T_r^3}{3} - \dfrac{CDT_r^4}{2} - \dfrac{D^2 T_r^5}{5}$

Tr is the reduced temperature (T/T$_{critical}$)

2, 3, or 4 coefficients must be specified and the critical temperature must be specified for this component.

TEMPERATURE DEPENDENT PROPERTIES IN NON-DIPPR EQUATION FORMS

Antoine Vapor Pressure-This equation is used if the program doesn't find coefficients for the DIPPR equation. P is in (mmHg), temperature (T) is in Kelvin.

$$Ln(P) = A - B/(T + C)$$

Ideal Gas Heat Capacity-Units of Cp are (cal/gmol-K), temperature (T) is in Kelvin. A through F are constants for the equation in the form.

$$Cp = A + BT + CT^2 + DT^3 + ET^4 + FT^5$$

This form is called the "Polynomial Ideal Gas Heat Capacity" equation and it is the program default.

Henry's Gas Law - The following equation is used to calculate Henry's constants for gases in liquid at low pressures:

$$lnH = A/T + B^* lnT + C^* T + D$$

where   H   =   Henry's constant, in psia per unit mole fraction of gas
        T   =   system temperature in degrees Rankine

A, B, C, D are the coefficients.

The coefficients are available for the following gases in water:

Hydrogen   Sulfur dioxide
Helium   Nitrous oxide
Argon   Chlorine
Neon   Bromine
Krypton   Iodine
Xenon   Methane
Oxygen   Ethane
Nitrogen   Propane
Hydrogen sulfide   Ethylene
Carbon monoxide   Ammonia
Carbon dioxide

The Henry's Gas Law is used:

1.   If selected as the K-Value option

2.   If selected as the K-Value option for supercritical components when activity coefficient methods are being used.

3.   In the Sour Water K-Value model

The Two Parameter Liquid Viscosity Equation: The following equation yields liquid viscosity in Cp. Temperature is in Kelvin.

$$Log(ViscL) = A(1/T - 1/B)$$

This equation is used as an alternate to the DIPPR equation.

The Two Parameter Surface Tension Equation: The following equation is used as an alternate to the DIPPR equation:

$$ST = A(1-Tr)^B$$

where   ST   =   surface tension in Newtons / meter
         Tr   =   reduced temperature
         A,B =   user supplied coefficients

USER SPECIFIED TRANSPORT PROPERTIES

For convenient customization, CHEMCAD lets the user utilize his/her own transport property equation. For all library transport properties, an equation number > 1000 indicates that the user specified equation will be used.

A text file corresponding to the specified equation number must be created by the user. The file name for this file is as follows: UsrEqnXXXX.sf(or .pf .uf) where XXXX is the equation number > 1000. The extension (.sf, .pf or .uf) of this file uses the CC5 file extension convension and determines the accessibility of this file. For example if .sf is used and the file is in CC5 program directory, the specified file can be used for all CC5 jobs. If .uf is used and the files are placed under the work folder, the files can be accessed by all jobs under the work folder.

The user can find a sample file UsrEqn1001.sf in the CC5 directory that can be used as a template for creating new user equation files. The file uses the CC5 build-in parser C language to describe the equation. Variables T, P, Tc, Pc, A, B, C, D, E and X have been declared internally by CHEMCAD and must not be re-declared in the file. In most cases, only one line in the file (such as X = A + B * log(T) + C * T + D * T * T + E / T) will be sufficient for the desired calculation. If additional variables are required, these variables must be declared the same way as the C language (See CC5 parser documentation).

A printout of the sample file UsrEqn1001.sf is shown below:

```
// Calculate user specified property by the following equation (Equation 1001 in this example)
// The property value X is defined as a function of
// 1. T  Temperature in degree K
// 2. P  Pressure in Pascal (optional)
// 3. Tc Critical temperature of the component, degree K (optional)
// 4. Pc Critical pressure of the component, Pascal (optional)
// 5. DIPPR Coefficients A, B, C, D and E as defined in CHEMCAD component database
// The engineering unit of return value X has the same definition as DIPPR database
//    Density : kmol/m3
//    Vapor pressure: pascals
//    Heat of vaporization: J/kmol
```

//   Heat capacity: J/kmol/K
//   Viscosity: pascal-sec
//   Thermal conductivity: W/m-K
//   Surface tension: N/m
//
X = A + B * log(T) + C * T + D * T * T + E / T;

PHYSICAL PROPERTY USES AND REQUIREMENTS IN CHEMCAD

In order to properly use the unit operation thermodynamic and transport property models available in CHEMCAD, the user should know what physical properties are used by each model. This chapter is intended to provide a cross reference so the user can quickly determine what properties are needed for a particular model. Six sections are provided (in tabular form) to summarize what models each property is used in; and which properties are required by each model.

The following sections are provided below:

- General property uses in CHEMCAD
- Physical properties and their uses in CHEMCAD
- Physical properties requirements of the K-Value Methods
- Physical property requirements of the Enthalpy Methods
- Physical properties required for distillation calculations
- Physical properties required by the reactor models

GENERAL PROPERTY USES IN CHEMCAD

This section provides a general summary of where the most commonly accessed properties are used in CHEMCAD. Column one gives the property name. Column two lists all of the ways CHEMCAD makes use of that property.

PROPERTY	USE(S)
Vapor Pressure	Calculate phase equilibrium by gamma and ideal vapor pressure.
Liquid Density	Calculate concentration terms in reaction rate equation (s).
	Calculate liquid volumes in vessels.
	Calculate liquid volume flowrates in streams.
	Calculate pump HP requirements.
	Calculate heat transfer film coefficients in CCT and CCR.
	Calculate ΔP in PIPE, CCT, and columns.
	Calculate relief valve sizes and/or flowrates.
	Calculate control valve and orifice sizes.
Vapor Density	Calculate vapor volume in vessels.
	Calculate pressure in vessels.
	Calculate vapor volume flowrate.
	Calculate compressor HP requirement.
	Calculate heat transfer coefficients in CCT.
	Calculate ΔP in PIPE, CCR, and columns.
	Calculate relief valve sizes and/or flowrates.

	Calculate control valve and orifice sizes.
Liquid Viscosity	Calculate ΔP in PIPE, CCT, and columns. Calculate heat transfer film coefficients in CCT and CCR. Calculate sizes of sieve trays. Calculate liquid diffusion coefficients for mass transfer.
Vapor Viscosity	Calculate ΔP in PIPE, CCT and columns. Calculate heat transfer film coefficients in CCT.
Liquid Thermal Conductivity	Calculate heat transfer film coefficients in CCT and CCR.
Vapor Thermal Conductivity	Calculate heat transfer film coefficients in CCT.
Liquid Heat Capacity	Calculate heat balance using LATE. Calculate ΔHr in batch reactor. Calculate heat transfer coefficients in CCT and CCR.
Vapor Heat Capacity	Calculate heat balance. Calculate heat transfer coefficients in CCT.
Surface Tension	Calculate heat transfer coefficients in CCT. Calculate ΔP in columns.
Heat of Formation	Enthalpy datum. Calculate ΔHr in reactors.
Gibbs Free Energy of Formation	Calculate reaction equilibrium in GIBS.
Heat of Vaporization	Calculate heat balance using LATE. Calculate heat transfer coefficients in CCT. Calculate ΔHr in batch reactor(s).
Critical Properties and Acentric Factor	Calculate phase equilibrium for EOS. Calculate enthalpy departure functions. Calculate vapor density.

PHYSICAL PROPERTIES AND THEIR USES IN CHEMCAD SIMULATIONS

This second table is a more comprehensive and specific restatement of the first. Column one lists the properties provided in the CHEMCAD database. Column two lists the ways CHEMCAD uses these properties. Column three lists the specific equations and models which use each property

PROPERTY	USE (S)	EQUATION (S)
Critical Temperature	Calculate K-Values by EOS. Calculate enthalpy departure function by EOS. Calculate liquid density. Calculate gas viscosity.	

	Calculate liquid viscosity.	Letsou & Stiel
Critical Pressure	Calculate K-Values by EOS. Calculate enthalpy departure function by EOS. Calculate liquid density. Calculate gas viscosity. Calculate liquid viscosity.	PR, SRK, APISRK, BWRS, ESD, SAFT, GS, MSRK TSRK API, Rackett Thodos Letsou & Stiel
Critical Volume	Calculate K-Values by EOS. Calculate enthalpy departure function by EOS.	BWRS BWRS
Melting Point	Not used	
Normal Boiling Point	Calculate K-Value by ESSO equation. Calculate ΔHv	ESSO Watson equation
IG Heat of Formation	Enthalpy datum. Calculate heat of reaction.	
IG Free Energy of Formation	Calculate reaction equilibrium in GIBS.	
Acentric Factor	Calculate K-Value by EOS. Calculate enthalpy departure function by EOS. Calculate liquid viscosity.	PR, SRK, APISRK, BWRS ESD, SAFT, MSRK, TSRK PSRK, GS Letsou & Stiel
Solubility Parameter	Calculate K-Value by gamma.	Regular, Florry-Huggins
Dipole Moment	Calculate gas viscosity.	Chapman-Euskog
Mean. Avg. Boiling Point		
Heat of Vaporization	Calculate latent heat in heat balance if DIPPR not present. Calculate heat of formation at system conditions (and therefore heat of reaction) if DIPPR not present.	LATE
API Net Heating Value	Stream properties printout.	
API Gross Heating Value	Stream properties printout	
Liquid Volume Constant	Calculate liquid density.	Cavett
Molecular Diameter	Calculate gas viscosity.	Chapman-Euskog

Modified Acentric Factor	Calculate α	Boston-Mathias
UNIQUAC Area Parameter	Calculate K-Value by gamma.	UNIFAC, UNIQUAC
UNIQUAC Volume Parameter	Calculate K-Value by gamma.	UNIFAC, UNIQUAC
Wilson Molar Volume	Calculate K-Value by gamma.	Wilson, TK Wilson, HRNM
Stiel Polar Factor		
Rackett Constant	Calculate liquid density.	Rackett
Polar Parameter	Calculate polar gas viscosity.	Brokaw
Eps / K	Calculate polar gas viscosity.	Neufeld
Watson Factor	Calculate K-Value by ESSO.	ESSO, Brokaw
API Gravity		
Specific Gravity		
Electrolyte State	Identifies solid electrolyte species which are handled differently.	
Electrolyte Type	Selection of parameters for calculation of activity and elect. reaction equilibrium	Pitzer
Electrolyte Charge	Maintain charge balance.	Electrolytes
Electrolyte Std. HT. of Formation	Calculate heat effects of ionization.	Electrolytes
Electrolyte Std. Free. Energy of Formation	Calculate elect. reaction equilibrium K	Electrolytes
Std. Entropy	Calculate elect. reaction equilibrium K	Electrolytes
Std. Heat Capacity	Calculate heat balance Calculate electrolyte reaction equilibrium K.	Electrolytes
Liquid Density Coefficients	Primary property method.	
Solid Density Coefficients	Not used.	
Vapor Pressure Coefficients	Primary property method.	
Heat of Vaporization Coefficients	Primary property method.	

Ideal Gas Heat Capacity Coefficients	Alternate equation for calculating vapor enthalpies.	
Liquid Heat Capacity Coefficients	Liquid enthalpies by LATE.	
Solid Heat Capacity Coefficients	Solid enthalpies	
Vapor Viscosity Coefficients	Primary property method.	
Liquid Viscosity Coefficients	Primary property method.	
Vapor Thermal Cond. Coefficients	Primary property method.	
Liquid Thermal Cond. Coefficients	Primary property method.	
Liquid Surface Tension Coefficients	Primary property method.	
Antoine VP Coefficients	If DIPPR not present.	
Polynomial IG Heat Capacity Coefficients	Primary property equation for vapor enthalpies.	
Two-Term Liquid Viscosity Coefficients	Used if DIPPR coefficients for liquid viscosity are not present.	
Two-Term Surface Tension Coefficients	Used if DIPPR coefficients for surface tension are not present.	
Henry's Constants	K-Values for light gases. K-Values for supercritical components.	
MSRK Parameters	K-Values by MSRK. Enthalpy departures function by MSRK.	MSRK
UNIFAC Sub-Groups	Calculate K-Value by gamma.	UNIFAC, UNIQUAC

PHYSICAL PROPERTY REQUIREMENTS OF THE K-VALUE METHODS

The following table summarizes the physical properties required to use each of the K-Value models in CHEMCAD.

- Column one gives the K-Value model name or acronym
- Column two identifies the type of equation the model is. A model may be of types:
  - i. Activity (activity coefficient model)
  - ii. Equation-of-state
  - iii. Ideal (ideal solution)
  - iv. Empirical (pure data fit)
  - v. User added (data or model supplied by the user)
- Column three lists the typical applications for the model
- Column four gives he physical properties used by that K-Value model

K-VALUE METHOD	TYPE OF MODEL	TYPICAL APPLICATIONS	REQUIRED PHYSICAL PROPERTIES
ACTX	Activity		
ADDK	User Added		
Amine	Empirical	DEA & MEA acid gas removal	
API SRK	Equation-of-State	Hydrocarbons	T_c, P_c, Ω, sometimes kij
BWRS	Equation-of-State	Light Hydrocarbons	T_c, P_c, Ω, sometimes kij
ESD	Equation-of-State	Polymers and strongly H-Bonded chemicals	T_c, P_c, Ω, sometimes BIPs
ESSO		Heavy Hydrocarbons (asphalts)	T_b, K
Florry-Huggins	Activity	Polymers	V_i, δ
GMAC (Chien-Null)	Activity	Polar mixtures, VLE & LLE	
Grayson-Stread	Empirical Equation-of-State	Hydrocarbons (refineries)	T_c, P_c, δ, Ω
Henry's Law	Empirical	Light (non-condensible) gases	Coefficients of equation
HRNM Modified Wilson	Activity	Alcohol systems, VLE & LLE	V_i, coefficients of VP equation, BIPs
Ideal Vapor Pressure	Ideal		Coefficients of VP equation
K-Table	User data		Pr, Ki .v. Temp.
Margules	Activity	Polar mixtures, VLE & LLE	Coefficients of VP equation

K-VALUE METHOD	TYPE OF MODEL	TYPICAL APPLICATIONS	REQUIRED PHYSICAL PROPERTIES
Modified UNIFAC	Activity	Polar mixtures, VLE & LLE	UNIFAC groups, BIPs, coefficients of VP equation
MSRK	Equation-of-state	Chemicals	Tc, Pc, m, n
NRTL	Activity	Polar mixtures, VLE & LLE	Coefficients of VP equation, BIPs
Peng-Robinson	Equation-of-state	Hydrocarbons and non-polar chemicals	Tc, Pc, Ω, sometimes kij
USRK	User data		K-Values and .ktb files.
Polynomial K	User data		Polynomial coefficients
PPAQ	User data	Single electrolyte systems (aqueous)	Partial pressure .v. T &C
PSRK	Equation-of-state & activity	Chemicals	Tc, Pc, Ω, UNIFAC groups
Regular Solution	Activity	Hydrocarbons	Vi, δ
SAFT	Equation-of-state	Polymers	Tc, Pc, Vs, SFs, DE/k, sometimes BIPs, property of polymers
Sour Water	Empirical	Acid gases dissolved in water	
SRK	Equation-of-state	Hydrocarbons	Tc, Pc, Ω, sometimes kij
TEG Dehydration	Empirical	Removal of water from hydrocarbons	
T. K. Wilson	Activity	Polar mixtures, VLE & LLE	Vi, coefficients of VP equation, BIPS
TSRK	Equation-of-state	Light gases dissolved in methanol	Tc, Pc, Ω, kij, ci
UNIFAC	Activity	Polar mixtures, VLE & LLE	UNIFAC groups, coefficients of VP equation
UNIFAC Polymers	Activity	Polymers	Vi, Ci, UNIFAC groups
UNIQUAC	Activity	Polar mixtures, VLE & LLE	q, r, coefficients of VP equation, BIPs
UNIQUAC / UNIFAC	Activity	Polar mixtures, VLE & LLE	q, r, coefficients of VP equation, BIPs
UNIFAC LLE	Activity	Polar mixtures, LLE	UNIFAC groups, coefficients of VP equation

K-VALUE METHOD	TYPE OF MODEL	TYPICAL APPLICATIONS	REQUIRED PHYSICAL PROPERTIES
VAN LAAR	Activity	Polar mixtures, VLE	coefficients of VP equation, BIPs
WILSON	Activity	Polar mixtures, VLE	Vi, coefficient of VP equation, BIPs

Legend: Tc   =   Critical temperature
         Pc   =   Critical pressure
         Vc   =   Critical volume
         Ω =   Acentric factor
         q   =   Surface parameter
         r   =   Volume parameter
         δ =   Solubility parameter
         K   =   Watson-Nelson factor
         Vi   =   Liquid molar volume
         BIPs =   Binary interaction parameters
         m,n   =   MSRK parameters
         kij   =   Binary interaction parameters for EOS
         Ki   =   Component K-Value
         T_b =   Normal boiling temperature
         C_w =   Third parameter for HRNM Wilson
         Pr   =   Reference pressure
         VP   =   Vapor pressure
         Vs   =   SAFT characteristic volume
         SFs   =   SAFT shape factor
         DE/k =   SAFT distribution energy
         Ci   =   Adjustable factor for UNIFAC for polymers

PHYSICAL PROPERTY REQUIREMENTS OF THE ENTHALPY METHODS

The following table summarizes the physical properties required to use each of the enthalpy models provided by CHEMCAD:

- Column one gives the enthalpy model name or acronym
- Column two lists the typical applications for the model
- Column three gives the physical properties used by the enthalpy model

ENTHALPY METHOD	APPLICATIONS	REQUIRED PHYSICAL PROPERTIES
Latent Heat	Non-ideal mixtures	Liquid heat capacity, heat of vaporization, ideal gas heat capacity
Equations-of-state: PR, SRK, APISRK, RK, MSRK, GS, BWRS, LK	Hydrocarbons and non-polar hydrocarbon chemicals	Tc, Pc, Ω, ideal gas heat capacity, sometimes kij
Amine	MEA and DEA acid gas removal systems.	
Mixed	To combine LATE and EOS methods.	
ADDH, H Table, Polynomial H	User added data and/or methods.	

PHYSICAL PROPERTIES REQUIRED FOR DISTILLATION CALCULATIONS IN CHEMCAD

Distillation calculations performed in CHEMCAD fall into the following categories:

- Phase equilibrium calculations
- Mass transfer calculations
- Tray sizing/rating calculations
- Packing hydraulic calculations

The component physical property requirements for these calculations are discussed below:

1. **Phase Equilibrium Calculations**

    The property requirements for distillation phase equilibrium calculations are the same as those for any other phase equilibrium calculation and are determined by the K-Value and enthalpy models selected. Please refer to those sections.

2. **Mass Transfer Calculations**

    Distillation mass transfer models in CHEMCAD require all of the properties necessary for phase equilibrium calculations plus those properties needed to calculate diffusion coefficients. Gas phase diffusion coefficients are affected by the following component physical properties:

    i. the molecular formula (if present) and the atoms (only for certain atoms if present)
    ii. the critical properties (Tc, Pc, Vc) whenever the conditions of (i) above are not met
    iii. the Lennard-Jones potential, E/k_B, if present
    iv. the molecular weight

    Liquid phase diffusion coefficients are affected by the following component physical properties:

    i. molecular weight
    ii. liquid viscosity

    iii. liquid molar volume
    iv. liquid activity coefficient

3. **Tray Sizing/Rating Calculations Use the Following Component Physical Properties:**

Item	Valve Trays	Bubble Cap Trays	Sieve Trays
Molecular weight	√	√	√
Liquid density	√	√	√
Liquid viscosity			√
Surface Tension		√	√
Tc, Pc, Ω *	√	√	√

*Only where EOS is used to calculate the vapor density. If the vapor phase is assumed to be ideal, the critical properties have no effect upon these calculations.

√ indicates the property is used in this calculation.

4. **Packing Hydraulics Calculations Use the Following Component Properties:**

    i. molecular weight
    ii. liquid density
    iii. liquid viscosity
    iv. surface tension
    v. vapor viscosity
    vi. Tc, Pc, and eccentric factor if the vapor phase is modeled using an equation of state.

PHYSICAL PROPERTIES REQUIRED BY REACTOR MODELS

1. **Properties for Calculations Common to all Reactor Models:**

    Certain calculations are performed by all reactor models. These include:

    i. Flash calculations
    ii. Determination of heat of reaction
    iii. Heat balance calculations

    The physical property requirements for the calculations are the same irrespective of what reaction model is being used. Those required for (i) flash calculations and (iii) heat balance calculations are determined by the thermodynamic models selected and are addressed elsewhere. Property requirements for the following reactor calculations are discussed below:

    i. Heat of reaction
    ii. Stoichiometric reactions
    iii. Equilibrium reactions-empirical
    iv. Equilibrium reactions- free energy
    v. Kinetic reactions
    vi. Heat transfer

2. **Heat of Reaction**

    Heat of reaction is reported in the REAC, EREA, KREA, and BREA reactor models. In the first three ΔHr is reported at standard conditions and is calculated as:

$$\Delta H_r^o \, (IG) = \Sigma \Delta H_f^o \, (IG, \text{products}) - \Sigma \Delta H_f^O \, (IG, \text{reactants})$$

For the batch reactor model, BREA, the heat of reaction is calculated and reported at system conditions. Since BREA only handles liquid phase reactions, the heat of vaporization must be deducted from the standard heat of formation. In addition, some sensible heat effects are possible.

$$\Delta Hr = \Sigma \Delta H_f \, (\text{Products})_{T,P} - \Sigma \Delta H_f \, (\text{Reactants})_{T,P}$$

where, $\Sigma \Delta H_f \, (\text{Products})_{T,P}$ = heat of formation of the products at system temperature and pressure.

$\Sigma \Delta H_f \, (\text{Reactants})_{T,P}$ = heat of formation of the reactants at system temperature and pressure.

By convention BREA always adopts the latent heat method to compute ΔHr. To perform this calculation, the program needs the following physical properties information for each species:

   i.   Standard IG heat of formation (25°C)
   ii. Heat of vaporization
   iii. Liquid heat capacity

3. **Stoichiometric Reactions**

   Stoichiometric reactions can be specified in the REAC (stoichiometric) reactor and in the EREA (equilibrium) reactor unit operations. Other than information related to heat of reaction, the only physical properties required for this type of reaction are the molecular weight and those properties necessary to perform the exiting flash at the end of the UnitOp (see flashes).

4. **Equilibrium Reactions-empirical**

   Reaction equilibrium can be calculated empirically or using Gibbs free energy minimization. The latter method is explained below.

   The empirical calculation of reaction equilibrium can be calculated by the following UnitOps:

   EREA-Equilibrium reactor
   SCDS-Simultaneous correction distillation

   In both cases the equilibrium model is the same. For the generic reaction:

$$rR + sS \ldots = pP + qQ \ldots$$
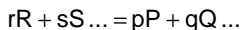
$$Ke = \frac{a_P^p \cdot a_{Q\ldots}^q}{a_R^r \cdot a_S^s \ldots}$$

$$\ln Ke = A + \frac{B}{T}$$

where	a	=	Species activity. Concentration for liquid phase reactions and partial pressure for vapor phase reactions.
	P,Q…	=	Products species
	R,S…	=	Reactant species
	p,q,r,s	=	Exponent (order) of species
	T	=	System temperature

       A,B   =   Correlated parameters

Physical properties required for this type of reaction are:

- For liquid phase reactions:
    i. Molecular weight to calculate the stoichiometry
    ii. Liquid density to calculate the concentrations
- For gas phase reactions:
    i. Molecular weights to calculate the stoichiometry

Partial pressure = (vapor mole fraction) • (system pressure) both of which are calculated in the flash calculation.

5. **Equilibrium Reactions by Gibbs Free Energy Minimization**

Reaction equilibrium can be calculated by Gibbs free energy minimization using the GIBS UnitOp. This reactor requires no stoichiometry to be defined. It maintains an atom balance during the simulation. The following physical properties are used to perform this calculation:

i. Molecular formulas-to maintain an atom balance
ii. Stand IG gibbs free energy of formation
iii. Ideal gas heat capacity
iv. Heat of vaporization (if the reaction is liquid phase and the latent heat enthalpy method is being used)
v. Liquid heat capacity (if the reaction is liquid phase and the latent heat enthalpy method is being used)

6. **Kinetic Reactions**

Reaction kinetics can be calculated in the following locations in CHEMCAD:

- The KREA (kinetic) reactor
- The SCDS distillation unitop
- The batch reactor
- The rate regression facility

The following general model is used:

$$rR + sS + \cdots \rightarrow pP + qQ + \cdots$$
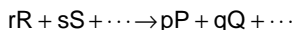
$$\text{rate} = A \bullet e^{-E/RT} \bullet [R]^{r^1} \bullet [S]^{s^1} \cdots \bullet [\text{Langmuir term}]$$

where

R,S,…	=	Reactants	
P,Q…	=	Products	
r,s,p,q,…	=	Stoichiometric coefficients	
$r^1, s^1, p^1, q^1,\ldots$	=	Reaction orders	
Rate	=	Reaction rate	
A	=	Frequency factor	
E	=	Activation energy	
[R],[S],…	=	The activities of the reactants. Concentrations for liquid phase reactions. Partial pressure for gas	

phase reactions.

| Langmuir term | = | A computed factor to account for the mass transfer resistance to and from a solid catalyst. |

To solve these equations, the program needs to know the following physical properties for each reaction constituent:

i. Molecular weight
ii. Liquid density (for liquid phase reactions) or partial pressure (for gas phase reactions)

Partial pressure = (vapor mole fraction) • (system pressure). Both of these are determined in the flash calculation.

7. **Heat Transfer Calculations (Batch Reactor, only)**

Calculations of film heat transfer coefficients in a batch reactor unit (BREA) involve calculation of the Reynolds number, the Prandtl number, the Nusselt number, and the viscosity ratio. The properties required for these are:

i.   Vapor Reynold's Nos.   -   Molecular weight and viscosity of the vapor constituents
ii. Liquid Reynold's Nos.   -   Molecular weight, viscosity, and density of the liquid components
iii. Vapor Prandtl Nos.   -   Molecular weight, heat capacity, thermal conductivity of the vapor components
iv. Liquid Prandtl Nos.   -   Molecular weight, heat capacity, thermal conductivity and density of the liquid components
v.   Viscosity Ratio   -   Liquid viscosity
vi. Vapor Nusselt Nos.   -   Thermal conductivity of the vapor components
vii. Liquid Nusselt Nos.   -   Thermal conductivity of the liquid components

BREA will only calculate a vapor coefficient on the jacket or coil side of the reactor.

SUMMARY OF PHYSICAL PROPERTIES REQUIRED BY REACTOR MODELS

	Heat of Reaction-at System Condition	Heat of Reaction-at Standard Condition	Stoichio metric Reactions	Equilibrium Reactions-Empirical	Equilibrium Reactions-Free Energy	Kinetic Reactions	Heat Transfer Calculations (Batch Reactor Only)
Molecular Weight	Required	Required	Required	Required		Required	Required
Std. IG heat of formation	Required	Required					

Std. IG Gibbs free energy of formation					Required		
IG heat capacity					Required if: EOS used for enthalpy Vapor is present		Required for Jacket (coil) fluids that are vapor
Liquid heat capacity	Required						Required
Heat of vapori-zation	Required				Required if LATE is used for Enthalpies		
Molecular formula					Required		
Liquid Viscosity							Required
Vapor Viscosity							Required for Jacket (coil) fluids that are vapor
Liquid thermal conductivity							Required
Vapor thermal conductivity							Required For Jacket (coil) fluids that are vapor
CHEMCAD Unit Operations	BREA	REAC, EREA, KREA	REAC EREA	EREA SCDS	GIBS	KREA SCDS BREA	BREA

ESTIMATING PURE COMPONENT PHYSICAL PROPERTIES

While the CHEMCAD databank is extensive, many users find the need to model a chemical which is not in the databank. Perhaps the user has a new chemical, or perhaps the user has a chemical which has never been properly studied in open literature. It is possible to create a new component for this chemical.

When a new component is created, a minimum amount of data is predicted for the chemical. If the user has valid data, entering the data into CHEMCAD is recommended.

Pure component physical properties can be estimated in four ways:

1.   Using the Hydrocarbon Pseudo Component Method
2.   Using the Joback Method
3.   Using the UNIFAC (Elliott) Method
4.   Inputting combustion solid data

The pseudo component method is a lumped component method usually applied to hydrocarbon mixtures. Properties are estimated from average molecular weight, specific gravity and/or normal boiling point using API oriented methods. The pseudocomponent method is meant for use with fairly simple straight chained hydrocarbons.

The Joback and Elliott methods are group contribution methods. These estimate properties from the functional groups contained in the molecule. The user selects a set of subgroups which can combine to form the molecule. The methods have additive contributions for each subgroup. For example, ethane could be predicted to have the effect of two –CH3 subgroups for boiling point, acentric factor, etc. Subgroup methods are most accurate when the molecule is a simple hydrocarbon. Subgroup models are generally more reliable than pseudo component methods for more complicated molecules.

The combustion solids option is a convenient method for defining a combustion solid from weight percent of elements. The method approximates properties important to combustion, so that the user may use the Gibbs reactor to simulate the burning process.

DEFINING A HYDROCARBON PSEUDO-COMPONENT

The hydrocarbon pseudo-component method is used for estimating properties for pseudo-components that may be constituents of pure hydrocarbon mixtures. This method is specifically for hydrocarbons in the form of lumped components. The method is empirical and requires only a minimal amount of information to generate reasonable properties for fractions.

The Pseudo-Component Method will estimate the following properties:

- Molecular weight (if not entered)
- Critical temperature
- Critical pressure
- Critical volume
- Acentric Factor
- Liquid volume constant
- Ideal gas heat capacity coefficients for the polynomial equation
- Solubility parameter
- Watson Factor

Only the average boiling point and specific gravity of the mixture are required input. The molecular weight will be estimated if the user does not input it.

Follow this procedure after selecting **New Component** from the **DATABANK MENU**.

1. Select pseudo-component and click OK.

2. The Component Name, Normal Boiling Point, and either the Specific Gravity or API Gravity **must** be entered. The molecular weight may be entered optionally.

3. Choose the correlation for estimating molecular weight. Select from:

    - Chemstations [Default]
    - Old API
    - New API
    - Lee Kesler

4. Choose the Critical Properties Method. Select from:

    - Cavett [Default]
    - API
    - Lee Kesler

5. Click **OK** to save data and the program will generate the properties and automatically call up the **Edit Component Menu**.

6. Use the **Edit Component Menu** to review data generated by the program and to change estimated data with any available experimental values.

MOLECULAR WEIGHT CORRELATIONS FOR PSEUDO COMPONENTS

The user can choose from any of four methods to calculate molecular weight (if not given) using the pseudo-component method. These are:

> The Chemstations Method (blend of the old and new API methods)
> The Old API Method
> The New API Method
> The Lee-Kesler Method

All four of these methods are described below.

THE CHEMSTATIONS METHOD FOR PSEUDOCOMPONENT MW

$$MW = 0.5(MW2 + MW3)$$

where   MW2   =   the Molecular Weight as calculated by the old API Method
               MW3   =   the Molecular Weight as calculated by the new API Method

If the MW as calculated above is greater than 250;

$$MW = \rho(\text{-}11.985 + 2.4966 * \log T_b - 1.174 * \log SG)$$

If the MW as calculated above is greater than 500;

$$MW = 0.5(W4 + MW3)$$

where, MW4 is the MW as calculated by the Lee-Kesler Method.

THE OLD API METHOD FOR PSEUDOCOMPONENT MW

$$MW = 204.38 * T_b^{0.118} * SG^{1.88} * \rho^{0.00218 * T_b} * \rho^{-3.07 * SG}$$

THE NEW API METHOD FOR PSEUDOCOMPONENT MW

$$MW = 20.486 * [\rho^{1.565\rho - 4 * T_b - 7.78712 * SG + 1.1582\rho - 3 * T_b * SG}] * T_b^{1.26} * SG^{4.983}$$

THE LEE-KESLER METHOD FOR PSEUDOCOMPONENT MW

$$MW = \text{-}12272.6 + 9486 * SG + (4.6523 - 3.3287 * SG) * T_b +$$
$$(1.0 - 0.77084 * SG - 0.02058 * SG^2] * \left(1.3437 - \frac{720.79}{T_b}\right) * \frac{187}{T_b} +$$
$$(1.0 - 0.80882 * SG + 0.0226 * SG^2)\left(1.8828 - \frac{181.98}{T_b}\right) * \frac{1.0\rho12}{T_b^3}$$

CRITICAL PROPERTIES FOR PSEUDOCOMPONENTS

CAVETT METHOD FOR PSEUDOCOMPONENT CRITICAL PROPERTIES

If the **Cavett Method** (default) is chosen by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$Tc = 768.0712 + 1.7133693 * T_b - 0.0010834 * T_b^2 -$$
$$0.008921258 * T_b * API + (3.8890584 \, \rho \text{-} 7) + T_b^3$$
$$5.309492 \, \rho - 6 * T_b^2 * API + 3.27116 \, \rho \text{-} 8 * (T_b * API)^2$$

$$\log Pc = 2.829046 + 0.0009412 * T_b - 3.047475 \, \rho - 5 * T_b^2 -$$
$$2.087611 \, \rho - 5 * API * T_b + 1.5184103 \, \rho - 9 * T_b^3 +$$
$$1.1047809 \, \rho - 8 * API * T_b^2 - 4.82716 \, \rho - 8 * API^2 * T_b +$$
$$1.3949619 \, \rho - 10 * (API * T_b)^2$$
$$Vc = \frac{Zc * Tc * 10.73}{Pc}$$

where　　Tc　=　Critical temperature in R
　　　　　Pc　=　Critical pressure in psia
　　　　　Zc　=　Critical compressibility factor calculated like so:

$$Zc = \frac{1}{3.43 + 6.7 \, \rho \text{-} 9 * \Delta^2}$$

and

$$\Delta = (8.75 + 1.987(\log T_b) + T_b)/1.8 \text{ if } Tc \langle 536.67 \, R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by f:

$$f = \left(\frac{Tc \text{-} 536.67}{Tc \text{-} T_b} \right)^{0.38}$$

if Tc > 593 R,

$$\Delta = \left(\frac{(0398907 * \text{specific gravity}) \, (\Delta \text{-} 592.4439)}{MW} \right)^{0.5}$$

$$\Omega = \frac{- \log Pc \text{ - } 5.92714 + 6.09648 / \theta \; + \; 1.28862 * \log \theta \text{ - } 0.169347 \, \theta^6}{15.2518 \text{ - } 15.6875 / \theta \text{ -} 13.4721 * \log^\Theta + 0.43577 * \theta^6}$$

where　　Pc　　Pressure in atm
　　　　　θ　　Normal boiling point/Critical temperature in R

The ideal gas heat capacity is calculated as follows:

α　　=　　$(0.036863384 * K - 0.4673722) * MW$
β　　=　　$(3.1865 \, \rho \text{ - } 5 * K + 0.001045186) * MW$
γ　　=　　$-4.9572 \, \rho \text{ - } 7 * MW$

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and

$$Cp_g = \alpha + \beta * T + \gamma * T^2 \ \text{ in } \ \frac{BTu}{lbmol\ R}$$

where Cp_g =   Ideal gas heat capacity
            T   =   System temperature in R

API METHOD FOR PSEUDOCOMPONENT CRITICAL PROPERTIES

If the **API Method** is selected by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$Tc = 24.2787 * T_b^{0.58848} * SG^{0.3596}$$

$$\ln Pc = \frac{3.12281\,\rho + 9}{T_b^{2.3125} * SG^{2.3201}} \ \text{ if } T_b \langle 1000°F, \text{ otherwise}$$

$$\ln Pc = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG}\right) + \left(\frac{0.11857}{SG^2}\right) * 0.001 * T_b$$

$$+ \left(1.4685 + \frac{3.648}{SG} + \left(\frac{0.47127}{SG^2}\right)\right) * I\,\rho - 7 * T_b^2 \ -$$

$$\left(0.42019 + \frac{1.6977}{SG^2}\right) I\,\rho - 10 * T_b^3$$

$$Vc = \frac{Zc * Tc * 10.73}{Pc}$$

where   Tc   =   Critical temperature in R
            Pc   =   Critical pressure in psia
            Zc   =   Critical compressibility factor calculated like so:

$$Zc = \frac{1}{3.43 + 6.7\,\rho - 9 * \Delta^2}$$

and,

$$\Delta = \left(8.75 + 1.987\left(\log T_b\right) * T_b\right)/1.8 \ \text{ if } \ Tc \langle 536.67\,R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by f:

$$f = \left(\frac{Tc - 536.67}{Tc - T_b}\right)^{0.38}$$

if Tc > 593 R,

$$\Delta = \left(\frac{(0.98907 * \text{specific gravity})(\Delta - 592.4439)}{\text{MW}} \right)^{0.5}$$

$$\Omega = \frac{-\log \text{Pc} - 5.92714 + 6.09648 / \theta + 1.28862 * \log \theta - 0.169347\, \theta^6}{15.2518 - 15.6875 / \theta - 13.4721 * \log^{\theta} + 0.43577 * \theta^6}$$

where   Pc   =   Critical pressure in atm
         θ =   Normal Boiling Point / Critical Temperature in R

The ideal gas heat capacity is calculated as follows:

         α = $(0.036863384 * K - 0.4673722) * \text{MW}$
         β = $(3.18565\, \rho - 5 * K + 0.001045186) * \text{MW}$
         γ = $-4.9572\, \rho - 7 * \text{MW}$

and

$$\text{Cp}_g = \alpha + \beta * T + \gamma * T^2 \text{ in} \frac{\text{BTu}}{\text{lbmol R}}$$

where Cp_g =   ideal gas heat capacity
         T   =   system temperature in R.

LEE-KESLER METHOD FOR PSEUDOCOMPONENT CRITICAL PROPERTIES

If the **Lee-Kesler Method** is selected by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$\text{Tc} = 341.7 + \frac{811}{\text{SG}} + (0.4244 + 0.1174\, \text{SG}) * T_b +$$

$$(0.4669 - 3.2623\, \text{SG}) * \frac{100,000}{T_b}$$

$$\ln \text{Pc} = 8.3634 - \frac{0.0566}{\text{SG}} - \left(0.24244 + \frac{2.2898}{\text{SG}} + \frac{0.11857}{\text{SG}^2} \right) *$$

$$0.00\ln T_b + \left(1.4685 + \frac{3.648}{\text{SG}} + \frac{0.47127}{\text{SG}^2} \right) * I\, \rho \text{-} 7 * T_b^2 -$$

$$\left(0.42019 + \frac{1.6977}{\text{SG}^2} \right) * I\, \rho \text{-} 10 * T_b^3$$

$$\text{Vc} = \frac{\text{Zc} * \text{Tc} * 10.73}{\text{Pc}}$$

where   Tc   =   Critical temperature in R
         Pc   =   Critical pressure in psia
         Zc   =   Critical compressibility factor calculated like so:

$$Zc = \frac{1}{3.43 + 6.7 \, \rho - 9 * \Delta^2}$$

and

$$\Delta = (8.75 + 1.987(\log T_b) * T_b)/1.8 \quad \text{if} \quad Tc \langle \ 536.67\,R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by, f;

$$f = \left(\frac{Tc - 536.67}{Tc - T_b} \right)^{0.38}$$

if Tc > 593 R,

$$\Delta = (8.75 + 1.987(\log T_b) * T_b)/1.8 \quad \text{if} \quad Tc \langle \ 536.67\,R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by, f;

$$f = \left(\frac{Tc - 536.67}{Tc - T_b} \right)^{0.38}$$

if Tc > 593 R,

$$\Delta = \left(\frac{(0.98907 * \text{specific gravity})(\Delta - 592.4439)}{MW} \right)^{0.5}$$

$$\Omega = \frac{-\log Pc - 5.92714 + 69648/\theta + 1.28862 \, \rho \, \log\theta - 0.169347\,\theta^6}{15.2518 - 15.6875/\theta - 13.4721 * \log\theta + 0.43577 * \theta^6}$$

where   Pc   =   Critical pressure in atm

θ =   Normal Boiling Point / Critical Temperature in R

The ideal gas heat capacity is calculated as follows:

α   =   (0.036863384 * K − 0.4673722) * MW
β   =   (3.1865 ρ - 5 * K + 0.001045186) * MW
γ   =   -4.9572 ρ - 7 * MW

and

$$Cpg = \alpha + \beta * T + \gamma T^2 \quad \text{in} \ \frac{BTU}{\text{lbmol R}}$$

where Cp_g =   ideal gas heat capacity
T   =   system temperature in R

DEFINING A COMPONENT WITH THE JOBACK/LYDERSON METHOD

The Joback Method is a group contribution method which will estimate the following properties:

- Molecular weight (if not given by the user)
- Critical temperature
- Critical pressure
- Critical volume
- Acentric Factor
- Normal boiling point (if not given by the user)
- Ideal gas heat of formation at 25°C and later.
- Ideal gas Gibbs Free Energy of Formation at 25°C and one atm
- Ideal gas heat capacity coefficients for the polynomial equation
- Solubility parameter
- Specific gravity at 60°F (if not given by the user)
- Heat of Vaporization at the normal boiling point
- Liquid volume constant
- Watson Factor

MOLECULAR WEIGHT BY THE JOBACK METHOD

Each functional group has a molecular weight of its own. Therefore, the molecular weight of the molecule is the sum of the molecular weights of the functional groups.

CRITICAL PROPERTIES BY THE JOBACK METHOD

One of the first very successful group contribution methods to estimate critical properties was developed by Lyderson in 1955. Joback reevaluated Lydersen's scheme, added several functional groups, and determined the values of the group contributions. His proposed relations are

$$T_c = T_b \left[0.584 + 0.965 \Sigma \Delta_T - (\Sigma \Delta_T)^2 \right]^{-1}$$

$$P_c = (0.113 + 0.0032 n_A - \Sigma \Delta_P)^{-2}$$

$$V_c = 17.5 + \Sigma \Delta_V$$

The units are Kelvin, Bar, and cubic centimeters per mole. n_A is the number of atoms in the molecule. The Δ values are given in Table 2-2.

NORMAL BOILING POINT BY THE JOBACK METHOD

A number of methods to estimate the normal boiling point have been proposed. More recent techniques are usually specific for a given homologous series as, for example, the work of Ambrose on alkanols. Others attempt to use London's theory to relate T_b to basic molecular parameters such as ionization potential, molar refraction, and shape. None in this latter class yield accurate estimations.

To obtain a very approximate prediction of T_b, one may use the group contributions for T_b in Table 4.1 with the relation:

$$T_b = 198 + \Sigma \Delta_b$$

where T_b is in Kelvin. The group increments were developed by Joback and these were tested on 438 diverse organic compounds. The average absolute error found was 12.9 K, and the standard deviation of the error was 17.9 K. The average of the absolute percent errors was 3.6%. Whereas these errors are not small, this simple technique may be useful as a guide in obtaining approximate values of T_b should no experimental value be available.

THERMOCHEMICAL PROPERTIES BY THE JOBACK METHOD

Choosing the same atomic and molecular groups as in Table 4.1 to estimate critical properties, Joback has used the values given in Stull et al. to obtain group contributions for ΔH_f^o (298 K), ΔG_f^o (298 K), and polynomial coefficients to relate C_p^o to temperature.

His group values are shown in Table 4.2 and they are to be used in the equations below.

With ΔH_f^o and ΔG_f^o in kJ/mol and C_p^o in J/(mol·K),

$$\Delta H_f^o \text{ (298K)} = 68.29 + \sum_j n_j \Delta_H$$

$$\Delta G_f^o \text{ (298K)} = 53.88 + \sum_j n_j \Delta_G$$

$$C_p^o = \left(\sum_j n_j \Delta_a - 37.93 \right) + \left(\sum_j n_j \Delta_b + 0.210 \right) T$$

$$+ \left(\sum_j n_j \Delta_c - 3.91 \times 10^{-4} \right) T^2 + \left(\sum_j n_j \Delta_d + 2.06 \times 10^{-7} \right) T^3$$

where n_j is the number of groups of the jth type and the Δ contributions are for the jth atomic or molecular group. The temperature T is in Kelvin.

Point Table 4.1 Joback Group Contributions for Critical Properties, the Normal Boiling Point, and Freezing

	Δ				
	T_c	P_c	V_c	T_b	T_f
Nonring groups:					
$-CH_3$	0.0141	-0.0012	65	23.58	-5.10
$>CH_2$	0.0189	0	56	22.88	11.27
$>CH-$	0.0164	0.0020	41	21.74	12.64
$>C<$	0.0067	0.0043	27	18.25	46.43
$=CH_2$	0.0113	-0.0028	56	18.18	-4.32
$=CH-$	0.0129	-0.0006	46	24.96	8.73
$=C<$	0.0117	0.0011	38	24.14	11.14
$=C=$	0.0026	0.0028	36	26.15	17.78
$\equiv CH$	0.0027	-0.0008	46	9.20	-11.18
$\equiv C-$	0.0020	0.0016	37	27.38	64.32

	Δ				
	T_c	P_c	V_c	T_b	T_f
Ring groups:					
–CH_2–	0.0100	0.0025	48	27.15	7.75
>CH–	0.0122	0.0004	38	21.78	19.88
>C<	0.0042	0.0061	27	21.32	60.15
=CH–	0.0082	0.0011	41	26.73	8.13
=C<	0.0143	0.0008	32	31.01	37.02
Halogen groups:					
–F	0.0111	-0.0057	27	-0.03	-15.78
–Cl	0.0105	-0.0049	58	38.13	13.55
–Br	0.0133	0.0057	71	66.86	43.43
–I	0.0068	-0.0034	97	93.84	41.69
Oxygen groups:					
–OH (alcohol)	0.0741	0.0112	28	92.88	44.45
–OH (phenol)	0.0240	0.0184	-25	76.34	82.83
–O– (nonring)	0.0168	0.0015	18	22.42	22.23
–O– (ring)	0.0098	0.0048	13	31.22	23.05
>C=O (nonring)	0.0380	0.0031	62	76.75	61.20
>C=O(ring)	0.0284	0.0028	55	94.97	75.97
O=CH– (aldehyde)	0.0379	0.0030	82	72.24	36.90
–COOH (acid)	0.0791	0.0077	89	169.09	155.50
–COO– (ester)	0.0481	0.0005	82	81.10	53.60
=O (except as above)	0.0143	0.0101	36	-10.50	2.08
Nitrogen groups:					
–NH2	0.0243	0.0109	38	73.23	66.89
>NH (nonring)	0.0295	0.0077	35	50.17	52.66
>NH (ring)	0.0130	0.0114	29	52.82	101.51
>N– (nonring)	0.0169	0.0074	9	11.74	48.84
–N= (nonring)	0.0255	-0.0099	—	74.60	—
–N= (ring)	0.0085	0.0076	34	57.55	68.40
–CN	0.0496	-0.0101	91	125.66	59.89
–NO_2	0.0437	0.0064	91	152.54	127.24
Sulfur groups:					
–SH	0.0031	0.0084	63	63.56	20.09
–S– (nonring)	0.0119	0.0049	54	68.78	34.40
–S– (ring)	0.0019	0.0051	38	52.10	79.93

Table 4.2 Joback Group Contributions for Ideal-Gas Properties

	Δ_H kJ/mol	Δ_G kJ/mol	Δ_a ••••••••••	Δ_b J/mol K	Δ_c ••••••••••	Δ_d
Nonring groups						
$-CH_3$	-76.45	-43.96	1.95E+1	-8.08E-3	1.53E-4	-9.67E-8
$>CH_2$	-20.64	8.42	-9.09E-1	9.50E-2	-5.44E-5	1.19E-8
$>CH-$	29.89	58.36	-2.30E+1	2.04E-1	-2.65E-4	1.20E-7
$>C<$	82.23	116.02	-6.62E+1	4.27E-1	-6.41E-4	3.01E-7
$=CH_2$	-9.63	3.77	2.36E+1	3.81E-2	1.72E-4	-1.03E-7
$=CH-$	37.97	48.53	-8.00	1.05E-1	-9.63E-5	3.56E-8
$=C<$	83.99	92.36	-2.81E+1	2.08E-1	-3.06E-4	1.46E-7
$=C=$	142.14	136.70	2.74E+1	5.57E-2	1.01E-4	-5.02E-8
$\equiv CH$	79.30	77.71	2.45E+1	2.71E-2	1.11E-4	-6.78E-8
$\equiv C-$	115.51	109.82	7.87	2.01E-2	-8.33E-6	1.39E-9
Ring groups						
$-CH_2-$	-26.80	-3.68	-6.03	8.54E-2	-8.00E-6	-1.80E-8
$>CH-$	8.67	40.99	-2.05E+1	1.62E-1	-1.60E-4	6.24E-8
$>C<$	79.72	87.88	-9.09E+1	5.57E-1	-9.00E-4	4.69E-7
$=CH-$	2.09	11.30	-2.14	5.74E-2	-1.64E-6	-1.59E-8
$=C<$	46.43	54.05	-8.25	1.01E-1	-1.42E-4	6.78E-8
Halogen groups						
$-F$	-251.92	-247.19	2.65E+1	-9.13E-2	1.91E-4	-1.03E-7
$-Cl$	-71.55	-64.31	3.33E+1	-9.63E-2	1.87E-4	-9.96E-8
$-Br$	-29.48	-38.06	2.86E+1	-6.49E-2	1.36E-4	-7.45E-8
$-I$	21.06	5.74	3.21E+1	-6.41E-2	1.26E-4	-6.87E-8
Oxygen groups						
$-OH$ (alcohol)	-208.04	-189.20	2.57E+1	-6.91E-2	1.77E-4	-9.88E-8
$-OH$ (phenol)	-221.65	-197.37	-2.81	1.11E-1	-1.16E-4	4.94E-8
$-O-$ (nonring)	-132.22	-105.00	2.55E+1	-6.32E-2	1.11E-4	-5.48E-8
$-O-$ (ring)	-138.16	-98.22	1.22E+1	-1.26E-2	6.03E-5	-3.86E-8
$>C=O$ (nonring)	-133.22	-120.50	6.45	6.70E-2	-3.57E-5	2.86E-9
$>C=O$ (ring)	-164.50	-126.27	3.04E+1	-8.29E-2	2.36E-4	-1.31E-7
$O=CH-$ (aldehyde)	-162.03	-143.48	3.09E+1	-3.36E-2	1.60E-4	-9.88E-8
$-COOH$ (acid)	-426.72	-387.87	2.41E+1	4.27E-2	8.04E-5	-6.87E-8
$-COO-$ (ester)	-337.92	-301.95	2.45E+1	4.02E-2	4.02E-5	-4.52E-8
$=O$ (except as above)	-247.61	-250.83	6.82	1.96E-2	1.27E-5	-1.78E-8

	Δ_H kJ/mol	Δ_G kJ/mol	Δ_a ••••••••	Δ_b J/mol K	Δ_c ••••••••	Δ_d
Nitrogen groups						
–NH$_2$	-22.02	14.07	2.69E+1	-4.12E-2	1.64E-4	-9.76E-8
>NH (nonring)	53.47	89.39	-1.21	7.62E-2	-4.86E-5	1.05E-8
>NH (ring)	31.65	75.61	1.18E+1	2.30E-2	1.07E-4	-6.28E-8
>N– (nonring)	123.34	163.16	-3.11E+1	2.27E-1	-3.20E-4	1.46E-7
–N= (nonring)	23.61	—	—	—	—	—
–N= (ring)	55.52	79.93	8.83	-3.84E-3	4.35E-5	-2.60E-8
=NH	93.70	119.66	5.69	-4.12E-3	1.28E-4	-8.88E-8
–CN	88.43	89.22	3.65E+1	-7.33E-2	1.84E-4	-1.03E-7
–NO$_2$	-66.57	-16.83	2.59E+1	-3.74E-3	1.29E-4	-8.88E-8
Sulfur groups						
–SH	-17.33	-22.99	3.53E+1	-7.58E-2	1.85E-4	-1.03E-7
–S– (nonring)	41.87	33.12	1.96E+1	-5.61E-3	4.02E-5	-2.76E-8
–S– (ring)	39.10	27.76	1.67E+1	4.81E-3	2.77E-5	-2.11E-8

ACENTRIC FACTOR BY THE JOBACK METHOD

The Joback method itself does not provide estimations for the acentric factor. When the Joback method is selected, CHEMCAD uses the Lee-Kesler method to estimate the acentric factor:

$$\omega = \frac{\alpha}{\beta}$$

where

$$\alpha = -\ln P_C - 5.97214 + 6.09648\,\Theta^{-1} + 1.28862\ln\Theta - 0.169347\Theta^6$$

$$\beta = 15.2518 - 15.6875\,\Theta^{-1} - 13.4721\ln\Theta + 0.43577\,\Theta^6$$

$$\Theta = \frac{T_b}{T_c}$$

$$P_C \,[=]\,atm.$$

HEAT OF VAPORIZATION BY THE JOBACK METHOD

When the Joback method is selected the following equation is used to estimate the heat of vaporization at the normal boiling point:

$$\Delta H_{v_b} = 1.093 R T_C \left[T_{b_r} \frac{(\ln P_C - 1)}{0.930 - T_{b_r}} \right]$$

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where ΔH_{v_b} =   the heat of vaporization at the normal boiling point

          R   =   the gas law constant
          T_c =   critical temperature
          P_c =   critical pressure
          T_{b_r} =   reduced normal boiling point $= \dfrac{T_b}{T_c}$

LIQUID VOLUME CONSTANT BY THE JOBACK METHOD

When the Joback method is selected, the liquid volume constant is estimated using the following procedure:

i.   Estimate the Rackett Constant, Z_{RA}:

$$Z_{RA} = 0.29056 - 0.08775\omega$$

ii.   Estimate the Liquid Molar Volume , V, at 77°F:

$$V = \frac{RT_c}{P_c}(Z_{RA})^{\left[1+(1-Tr)^{2/7}\right]}$$

iii.   Calculate the Liquid Volume Constant, LVC:

$$LVC = \frac{V}{\left(5.7 + \dfrac{1611}{T_c}\right)}$$

THE SPECIFIC GRAVITY AT 60°F BY THE JOBACK METHOD

The specific gravity at 60°F is calculated using the Cavett equation. The Cavett equation has the form:

$$\text{liquid volume } = \text{Vol Con} \ * \ (5.7 \ + \ 3Tr)$$

where   Liquid volume   =   is in cc/gmole
         Vol Con   =   Liquid mole volume constant
         Tr   =   Reduced temperature

The inverse of this value is divided by the density of water at 60°F to get the specific gravity.

SOLUBILITY PARAMETER BY THE JOBACK METHOD

The solubility parameter is calculated from its definition like so:

$$\delta = \left[\frac{\Delta H_v^{298}}{V_L}\right]^{0.5} \quad [=] \quad \left(\frac{cal}{°c}\right)$$

WATSON FACTOR BY THE JOBACK METHOD

The Watson Factor, K, is calculated like so:

$$K = \frac{(NBP)^{0.333}}{S.G.}$$

DEFINING A COMPONENT WITH THE UNIFAC (ELLIOTT) METHOD

The following method alternately called the "Elliott" or "UNIFAC" methods also estimate pure component physical properties from a tabulation of its functional groups. The method is called the "UNIFAC" method because it uses the same functional groups as the UNIFAC activity coefficient method.

CRITICAL PROPERTIES BY THE UNIFAC METHOD

Tc=Tb*[1+(1.28+ΣΔT)$^{-1}$]	[=] K
Pc=MW*(0.346+ΣΔP)$^{-2}$	[=] bars
Vc=172+ΣΔV	[=] cc/gmole
Tb=1000/(0.5+35.7/sqrt[ΣΔTb) +1000/(142+ΣΔTb)]	[=] K

THERMOCHEMICAL PROPERTIES BY THE UNIFAC METHOD

ELLIOTT GROUP CONTRIBUTION ESTIMATION FORMULAS IN CHEMCAD

Property	Equation	% error	Literature Source
$T_c\,[K]$	$T_b^{\,*}\left[1 + (1.28 + \Sigma\Delta_i)^{-1}\right]$	0.9	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
$P_c\,[bar]$	$MW^{\,*}(0.346 + \Sigma\Delta_i)^{-2}$	6.1	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
$V_c\,[cc/mol]$	$172 + \Sigma\Delta_i$	14.6	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
ω	$\Sigma\Delta_i$	20.1	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
$T_b\,[K]$ (760mmHg)	$1000/\left[0.5 + 35.7/(\Sigma\Delta_i)^{1/2} + 1000/(142 + \Sigma\Delta_i)\right]$	4.7	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
$T_b\,[K]$ (10mmHg)	$1000/\left[0.5 + 66/(\Sigma\Delta_i)^{1/2} + 1000/(158 + \Sigma\Delta_i)\right]$	3.6	Zuppo and Elliott, Ind. Eng. Chem. Res. Submitted (1999).
$H_{vap}\,(298)$ kJ / mole	$6.829 + \Sigma\Delta_i$	3.2	Constantinou & Gani, AIChEJ, 40: 1704 (1994).

$H_f^o(298)$	$10.835 + \Sigma\Delta_i$	8.3 kJ/mol	Constantinou & Gani, AIChEJ, 40: 1704 (1994).
$G_f^o(298)$	$-14.828 + \Sigma\Delta_i$	7.3 kJ/mol	Constantinou & Gani, AIChEJ, 40: 1704 (1994).
$T_m[K]$	$102.425 \exp(\Sigma\Delta_i)$	8.9	Constantinou & Gani, AIChEJ, 40: 1704 (1994).
$V^L(298)$	$\Sigma\Delta_i$	7.7	Fedors, Poly. End. Sci, 14:147 (1974) (cf. Van Krevelen, Elsevier, NY, 1990)
Cp^o	$A + BT + CT^2 + DT^3$		Joback, MIT thesis, Boston, 1984 (cf. Reid et al., Prop. Gas & Liq; 1987).
$\delta(cal/cc)^{1/2}$	$\left[\left(H_{vap} - 298R / V^L\right)\right]^{1/2}$		Definition
SG	MW / V^L		Definition

CRITICAL PROPERTIES BY THE UNIFAC METHOD

Critical properties are estimated by an adaption of the Ambrose method described by Reid et. al. (1987, pp.12, 13). The equations are of the form:

Equation	Units	Avg. % error
$T_c = T_b[1 + (1.28 + \Sigma\Delta_T)^{-1}]$	Kelvin	0.934
$P_c = M(0.346 + \Sigma\Delta_p)^{-2}]$	Bar	6.11
$V_c = 172 + \Sigma\Delta_v$	$Cm^3/gmole$	15

The group contributions have been regressed in terms of UNIFAC group contibutions since these are normally required by other parts of the CHEMCAD program. Note that the Lydersen/Joback method predicts negative values for the critical temperature at high molecular weights.

BOILING TEMPERATURE BY THE UNIFAC METHOD

$T_b = 1000/[0.5 + 35.7/sqrt(\Sigma\Delta_{TB}) + 1000/(142 + \Sigma\Delta_{TB})]$ [=] Kelvin; Avg. error = 4.67%

The form of this equation was suggested by a study of the critical point of the ESD equation of state in conjunction with the molecular simulations of the dePablo and coworkers, and the experimental studies of Schultz and Flory. All of these works indicate a dependency on the molecular weight that follows the reciprocal square-root + reciprocal form consistent with this equation. Other popular forms for the boiling temperature (e.g. Joback, Fedors, Gani) indicate improper asymptotic behavior at high molecular weights. The Lydersen and Joback methods even indicate negative boiling temperatures at high molecular weights. The group contributions have been regressed in terms of UNIFAC group contributions since these are normally required by other parts of the CHEMCAD program.

ENERGIES OF VAPORIZATION AND FORMATION BY THE UNIFAC METHOD

These correlations have been adopted without further review from the paper Gani, AIChE. J., 40:1704 (1994). First-order group contributions from conventional UNIFAC groups were well-defined in the correlations as reported. Interested readers are referred to the original article for more in-depth discussion of these methods.

Equation	Units
$H_v^{298} = 6.829 + \Sigma\Delta_{HV}$	kJ/gmole
$H_f^{298} = 10.835 + \Sigma\Delta_{Hf}$	kJ/gmole
$G_f^{298} = -14.828 + \Sigma\Delta_{Gf}$	kJ/gmole

The group contributions are taken from Table 4.3 below.

TABLE 4.3 GROUP CONTRIBUTIONS FOR THE UNIFAC METHOD

Values marked as "NA" are amides, for which we had no Tc values in the database. Values marked as "error" represent groups that correspond to a complete pure component, so they should not be treated as group contributions. "Error" values should prompt flags if users try to indicate these groups as part of a new component.

	rms%err=	0.934	6.112	15	4.67	These 3 from Gani, AIChEJ, 40:1704		
GRP ID	FORMULA	ΔT	ΔP	ΔV	ΔTb	Hf298	Gf298	Hv298
1	CH$_3$-	0.135	0.232	40	123	-45.947	-8.03	4.116
2	CH$_2$<	0.131	0.224	41	121	-20.763	8.231	4.65
2.5	RCH$_2$<	0.077	0.177	25	138	-20.763	8.231	4.65
3	CH	0.073	0.186	30	97	-3.766	19.848	2.771
3.5	>RCH-	0.070	0.195	37	107	-3.766	19.848	2.771
4	>C<	-0.015	0.143	5	74	17.119	37.977	1.284
4.5	>RC<	0.070	0.204	55	20	17.119	37.977	1.284
5	CH$_2$=CH	0.169	0.360	32	257	53.712	84.926	6.714
6	CH=CH	0.169	0.360	32	257	69.939	92.9	7.37
7	CH$_2$=C	0.169	0.360	32	257	64.145	88.402	6.797
8	CH=C	0.169	0.360	32	257	82.528	93.745	8.178
9	C=C	0.169	0.360	32	257	104.293	116.613	9.342
9.5	CH$_2$=C=CH	0.338	0.720	64	514	197.322	221.308	12.318
10	ACH	0.069	0.153	16	124	11.189	22.533	4.098
11	AC-	0.099	0.173	87	247	27.016	30.485	12.552
12	ACCH$_3$	0.221	0.375	68	282	-19.243	22.505	9.776
13	ACCH$_2$	0.207	0.370	95	303	9.404	41.228	10.185
14	ACCH	0.136	0.356	107	191	27.671	52.948	8.834
15	OH	0.554	0.075	-25	474	-181.422	-158.589	24.529
16	CH$_3$OH	error	error	error	—	—	—	—
17	H2O	error	error	error	—	—	—	—
18	ACOH	0.278	0.126	-20	525	-164.609	-132.097	40.246
19	CH3CO	0.387	0.513	77	514	-182.329	-131.366	18.999
20	CH2CO	0.383	0.504	78	512	-164.41	-132.386	20.041

TABLE 4.3 (CONT.) GROUP CONTRIBUTIONS FOR THE UNIFAC METHOD

GRP ID	FORMULA	ΔT	ΔP	ΔV	ΔTb	Hf298	Gf298	Hv298
21	CHO	0.299	0.324	-8	396	-129.158	-107.858	12.909
22	CH_3COO	0.457	0.712	102	451	-389.737	-318.616	22.709
23	CH_2COO	0.453	0.704	103	573	-359.258	-291.188	17.759
24	HCOO	0.305	0.455	-6	426	-332.822	-288.902	—
25	CH_3O	0.234	0.367	41	288	-163.569	-105.767	10.919
26	CH_2O	0.230	0.358	42	286	-151.143	-101.563	7.478
27	CH-O	0.175	0.311	27	262	-129.488	-92.099	5.708
28	FCH_2O	0.140	0.249	-57	323	-140.313	-90.883	11.227
29	CH_3NH_2	error	error	error	—	—	—	—
30	CH_2NH_2	0.301	0.316	78	437	-15.505	58.085	14.599
31	$CHNH_2$	0.247	0.269	62	412	3.32	63.051	11.876
32	CH_3NH	0.306	0.324	77	444	5.432	82.471	14.452
33	CH_2NH	0.301	0.316	78	442	23.101	95.888	14.481
34	CHNH	0.247	0.269	62	418	26.718	85.001	—
35	CH_3-RN	0.148	0.313	111	293	54.929	128.602	6.947
36	CH_2-RN	0.144	0.304	112	291	69.885	132.756	6.918
37	$ACNH_2$	0.270	0.211	24	655	20.079	68.861	28.453
38	C_5H_5N	error	error	error	—	—	—	—
39	C_5H_4N	0.433	0.869	107	942	134.062	199.958	31.523
40	C_5H_3N	0.433	0.869	107	942	139.758	199.288	31.005
41	CH_3CN	error	error	error	—	—	—	—
42	CH2CN	0.512	0.564	27	794	88.298	121.544	23.34
43	COOH	0.615	0.511	-31	858	-396.242	-349.439	43.046
44	HCOOH	error	error	error	—	—	—	—
45	CH_2CL	0.236	0.542	79	360	-73.568	-33.373	13.78
46	CHCL	0.178	0.504	68	336	-63.795	-31.502	11.985
47	CCL	0.090	0.461	43	313	-57.795	-25.261	9.818
48	CH_2CL_2	error	error	error	—	—	—	—
49	$CHCL_2$	0.283	0.822	107	575	-82.921	-35.814	19.208
50	CCL_2	0.196	0.779	82	552	—	—	17.574
51	$CHCL_3$	error	error	error	—	—	—	—
52	CCL_3	0.326	1.161	124	598	-107.188	-53.332	—
53	CCL_4	error	error	error	—	—	—	—
54	ACCL	0.165	0.460	47	358	-16.752	-0.50%	11.883
55	CH_3NO_2	error	error	error	—	—	—	—
56	CH_2NO_2	0.440	0.617	34	692	-66.138	17.963	30.644
57	$CHNO_2$	0.440	0.617	34	668	-59.142	18.088	26.277
58	$ACNO_2$	0.440	0.617	34	818	-7.365	60.161	—
59	CS_2	error	error	error	—	—	—	—
60	CH_3SH	error	error	error	—	—	—	—
61	CH_2SH	0.203	0.476	65	515	-8.253	16.731	14.931
62	FURFURAL	error	error	error	—	—	—	—
63	$<CH_2OH>_2$	error	error	error	—	—	—	—
64	I	0.056	0.816	-7	525	57.546	46.945	14.364

TABLE 4.3 (CONT.) GROUP CONTRIBUTIONS FOR THE UNIFAC METHOD

GRP ID	FORMULA	ΔT	ΔP	ΔV	ΔTb	Hf298	Gf298	Hv298
65	Br	0.056	0.522	6	353	1.834	-1.721	11.423
66	CH===C	0.125	0.274	-12	288	220.803	217.003	7.751
67	C===C	0.125	0.274	-12	288	227.368	216.328	11.549
68	ME$_2$SO	error	error	error	—	—	—	—
69	ACRY	error	error	error	—	—	—	—
70	CL<C=C>	0.082	0.318	23	190	-36.097	-28.148	
71	ACF	0.147	0.340	27	135	-161.74	-144.549	4.877
72	DMF-1	error	error	error	—	—	—	—
73	DMF-2	error	error	error	—	—	—	—
74	CF$_3$	0.340	0.886	188	141	-679.195	-626.58	8.901
75	CF$_2$	0.222	0.638	127	108	—	—	1.86
76	CF	0.103	0.391	66	91	—	—	8.901
77	COO	0.327	0.485	47	338	-313.545	-281.495	—
78	SiH$_3$	0.209	0.398	-6	164	—	—	—
79	SiH$_2$	0.205	0.298	41	164	—	—	—
80	SiH	0.151	0.251	25	164	—	—	—
81	Si	0.144	0.269	37	164	—	—	—
82	SiH$_2$O	0.245	0.675	108	44	—	—	—
83	SiHO	0.245	0.675	108	44	—	—	—
84	SiO	0.215	0.645	108	61	—	—	—
85	TERT-N	0.148	0.200	-15	225	—	—	—
86	CCL$_3$F	error	error	error	—	—	—	—
87	CCL$_2$F	0.314	1.027	143	569	-258.96	-209.337	13.322
88	HCCL$_2$F	error	error	error	—	—	—	—
89	HCCLF	0.209	0.709	104	477	—	—	—
90	CCLF$_2$	0.327	0.956	165	348	-446.835	-392.975	8.301
91	HCCLF$_2$	error	error	error	—	—	—	—
92	CCLF$_3$	error	error	error	—	—	—	—
93	CCL$_2$F$_2$	error	error	error	—	—	—	—
93.5	F (exceptions)	—	—	—	17	-223.398	212.718	—
94	CONH$_2$	0.422	0.372	73	707	-203.188	136.742	—
95	CONHCH$_3$	0.557	0.605	114	835	-67.778	—	—
96	CONHCH$_2$	0.553	0.596	115	833	-182.005	—	51.787
97	CON<CH$_3$>$_2$	0.670	0.946	101	862	-189.888	-65.642	—
98	CONCH$_3$CH$_2$	0.666	0.937	102	860	-46.562	—	—
99	CON<CH$_2$>$_2$	0.662	0.929	103	858	—	—	—
100	C$_2$H$_5$O$_2$	0.839	0.658	55	830	-344.125	241.373	—
101	C$_2$H$_4$O$_2$	0.609	0.761	109	495	—	—	—
102	CH$_3$S	0.207	0.485	64	473	-2.084	30.222	16.921
103	CH$_2$S	0.203	0.476	65	471	18.022	38.346	17.117
104	CHS	0.149	0.429	49	447	—	—	13.265
105	MORPH	error	error	error	—	—	—	—
106	C$_4$H$_4$S	error	error	error	—	—	—	—
107	C$_4$H$_3$S	0.379	0.960	125	0	—	—	27.966

TABLE 4.3 (CONT.) GROUP CONTRIBUTIONS FOR THE UNIFAC METHOD

GRP ID	FORMULA	ΔT	ΔP	ΔV	ΔTb	Hf298	Gf298	Hv298
108	C_4H_2S	0.372	0.978	137	0	—	—	—
109	NMP	error	error	error	—	—	—	—

ACENTRIC FACTOR BY THE UNIFAC METHOD

The Unifac method itself does not provide estimations for the acentric factor. When the Unifac method is selected, CHEMCAD uses the Lee-Kesler method to estimate the acentric factor:

$$\omega = \frac{\alpha}{\beta}$$

where

$$\alpha = -\ln P_c - 5.97214 + 6.09648\,\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6$$

$$\beta = 15.2518 - 15.6875\,\theta^{-1} - 13.4721\ln\theta + 0.43577\,\theta^6$$

$$\theta = \frac{T_b}{T_c}$$

$$P_c\ [=]\text{atm.}$$

LIQUID VOLUME CONSTANT BY THE UNIFAC METHOD

When the Unifac method is selected, the liquid volume constant is estimated using the following procedure:

i.   Estimate the Rackett Constant, Z_{RA}:

$$Z_{RA} = 0.29056 - 0.08775\omega$$

ii.   Estimate the Liquid Molar Volume , V, at 77°F:

$$V = \frac{RT_c}{P_c}\left(Z_{RA}\right)^{\left[1+(1-Tr)^{2/7}\right]}$$

iii.   Calculate the Liquid Volume Constant, LVC:

$$LVC = \frac{V}{\left(5.7 + \dfrac{1611}{T_c}\right)}$$

THE SPECIFIC GRAVITY AT 60°F BY THE UNIFAC METHOD

The specific gravity at 60°F is calculated using the Cavett equation. The Cavett equation has the form:

$$liquid\ volume\ =\ Vol\ Con\ *\ (5.7\ +\ 3Tr)$$

where   Liquid volume =   is in cc/gmole
         Vol Con   =   Liquid mole volume constant
         Tr   =   Reduced temperature

The inverse of this value is divided by the density of water at 60°F to get the specific gravity.

SOLUBILITY PARAMETER BY THE UNIFAC METHOD

The solubility parameter is calculated from its definition:

$$\delta\ =\ \left[\frac{\Delta H_v - 298R}{V_L}\right]^{0.5}\ \ [=]\ \ \left(\frac{cal}{°C}\right)^{0.5}$$

WATSON FACTOR BY THE UNIFAC METHOD

The Watson Factor, K, is calculated like so:

$$K = \frac{(NBP)^{0.333}}{S.G.}$$

DEFINING A COMBUSTION SOLID

The user may specify element types such as C,H O, S, Si and their weight percent when the actual formula of a combustion solid is unknown the elemental analysis is available. The combustion solid can be used to simulate burning reactions in a Gibbs reactor UnitOp. Heating value and heat capacity of the solid may also be given.

EXAMPLE: PHYSICAL PROPERTIES ESTIMATION FOR 1,1,2-TRIMETHYLCYCLOHEXANE

To illustrate the physical properties estimation procedure, let's estimate the physical properties of the component 1,1,2-Trimethylcyclohexane using the Joback Method.

We begin by selecting the **New Component** command from the **Databank Menu**, which is found on the **ThermoPhysical Menu** on the **Menu Bar**, like so:
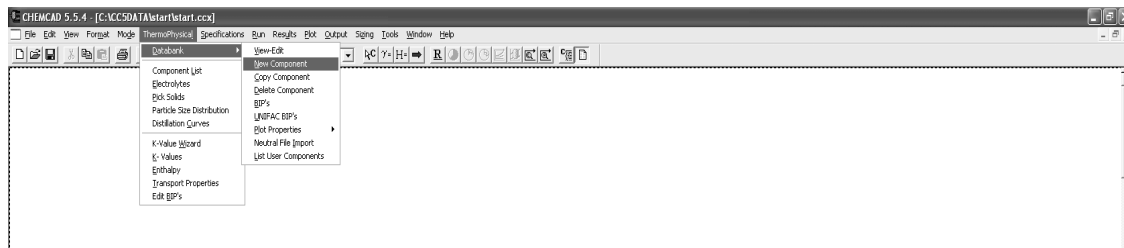
When you click on the **New Component** command, the **New Component dialog box** will appear. Since we are using the Joback Method, it should be completed as follows:

It is not required to supply the normal boiling point, but doing so will improve the accuracy of the estimates (provided, of course, that the NPB value is correct). After completing the dialog box, click the **OK** button.

The **Group Assignments dialog box** will appear. 1,1,2-Trimethylcyclohexane has the following groups:

3 non-ring methyl groups

1 ring >C< group

CH3   CH3

CH3

1 ring >CH- group

4 ring -CH2- groups
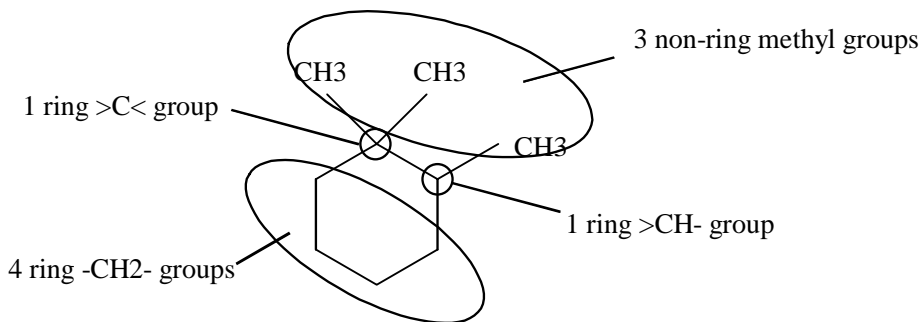
The **Group Assignments dialog box** should be completed as shown:

Upon clicking the **OK** button, the following dialog box will appear requesting confirmation.

Click **Yes**,and the following message box will appear:

Click **OK**. The program will now permit you to view and/or edit the results of the estimation by displaying the **View/Edit Component Data Menu**.
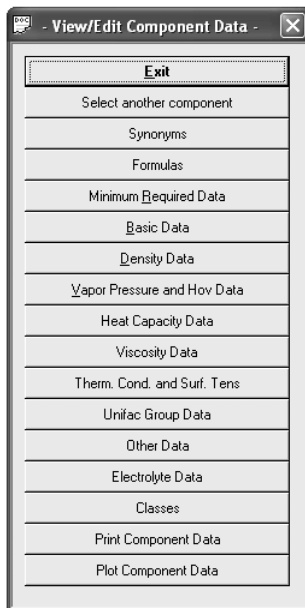
The bulk of the estimations will be stored under the **Basic Data dialog box**. Therefore, click on this item now.

PURE COMPONENT PHYSICAL PROPERTIES REGRESSION

PURE COMPONENT REGRESSION (TOOLS MENU)

This regression package lets you fit experimental data to obtain properties for pure components. Options are:

- Antoine Vapor Pressure
- DIPPR Vapor Pressure
- Heat of Vaporization
- Liquid Density
- Liquid Heat Capacity
- Liquid Viscosity
- Liquid Thermal Conductivity
- Liquid Surface Tension
- Ideal Gas Heat Capacity
- Vapor Viscosity
- Vapor Thermal Conductivity

Pure Component Physical Properties Regression Procedure:

1. Make sure the component whose properties are to be regressed is a <u>user added component</u>. If it is not, it will need to be copied into the user's databank because the user cannot edit CHEMCAD's standard components.

2. Select the **Pure Regression** option from the **Tools Menu** in the menu bar. A menu will appear, displaying the above list.

3. Select the property to be regressed from the menu.

4. CHEMCAD will display the component selection list. Find the component in the list and select it.

5. You will then get a dialog box that displays initial estimates, upper bound and lower bound for each coefficient. You may also adjust the maximum number of iterations and the convergence tolerance for the regression step.

6. Enter the experimental data in the dialog box provided by the program (it will automatically appear after the above dialog box is closed).

7. Click **[OK]** to accept the data and start the calculation.

8. Upon completion of the regression calculation, the results will be displayed in a **WORDPAD** file. This report will contain the following information:

    i. Whether or not the parameters are converged and/or minimized.
    ii. A comparison of the experimental data to the model's calculated results.
    iii. The mean and maximum deviations.
    iv. The calculated parameters.

9. Finally, a dialog box will appear asking if you want to save the regressed parameters or not. If you answer "yes" the parameters will be directly saved to the selected User Added Database Component.

EXAMPLE: REGRESS THE VAPOR PRESSURE OF 1,1,2-TRIMETHYLCYCLOHEXANE

To illustrate the process of regressing pure component physical properties data, let's compute the parameters of the DIPPR Vapor Pressure equation for 1,1,2-Trimethylcyclohexane. You will recall that this is the component for which we estimated properties using the Joback Method in a prior section of this manual.

The form for this equation is:

$$P = \exp[A + B/T\, C\ln T + DT^E]$$

A, B, C, D and E are the coefficients to be calculated from the data.

We have the following vapor pressure data for this compound:

Temperature, C	Pressure, Pa
-0.2	100
23.0	1000
71.5	10000
145.5	100000

Make sure your selected engineering units have Pascals for pressure and degrees C for temperature since the data is given in these units.

We begin by selecting the **Pure Regression** option on the **Tools Menu**.
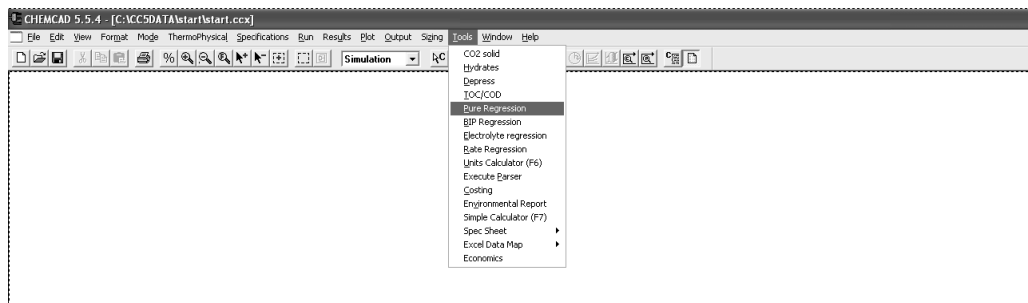
The program will respond by asking you what property you want regressed.
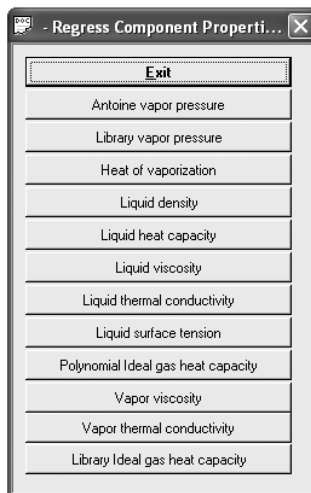
In our example, we want to calculate the parameters for the Library Vapor Pressure equation. Therefore, click on that option (the third button from the top). The **Component Selection dialog box** will appear. From the list at the right select the component 1,1,2-Trimethylcyclohexane:
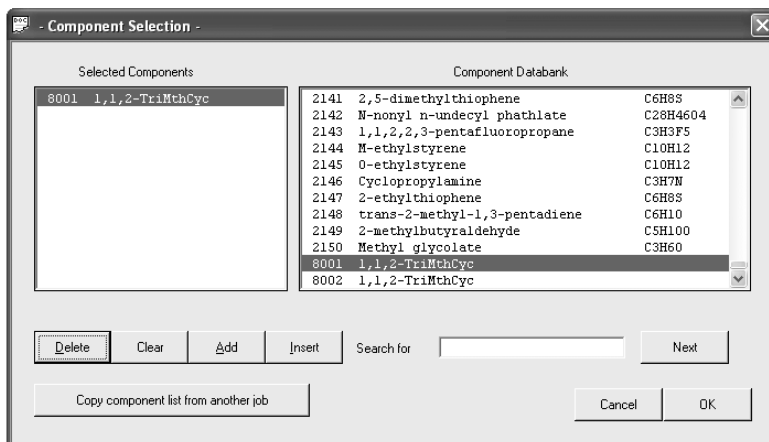
Upon clicking the **OK** button, the program will confirm your selection by displaying the following dialog box:
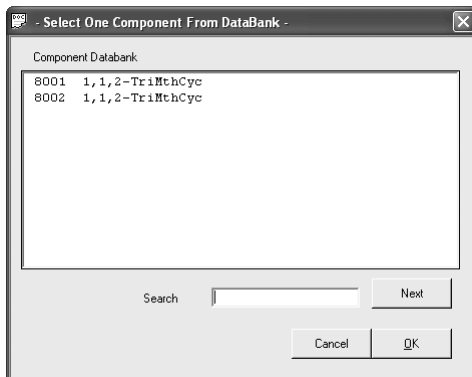
Click **OK** to confirm. This will take you to the **Library Vapor Pressure Parameters dialog box**.
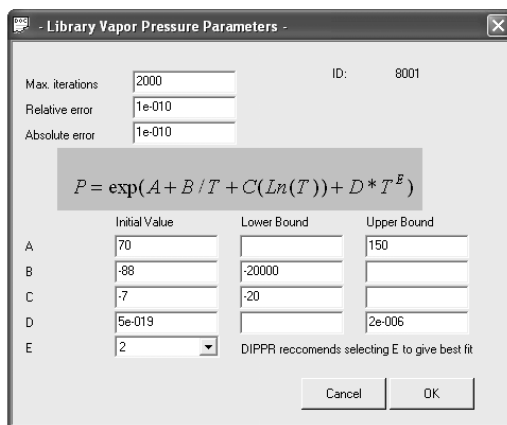
There is no need to enter or edit anything on this screen because:

i. The program has default values for:
- Maximum number of iterations (1000)
- Relative error (le-10)
- Absolute error (le-10)
- Lower bound
- Upper bound

ii. The program will make its own initial estimates.

Therefore, click the **OK** button. The **Vapor Pressure Data dialog box** will then appear. Using the data given above, it should be completed as shown:

Weight factors need not be given unless the user wants to give greater emphasis to certain data points. Otherwise, a default value of 1.0 is given to each data point.

Click **OK** and the regression calculation will begin. When the calculations are finished, the following output will automatically be reported in **WORDPAD**.

Close **WORDPAD** by clicking on the ☒ button in the upper right hand corner of the **WORDPAD** dialog box. A message box will appear, asking if you want to save the regressed parameters. When you click **OK**, these parameters will automatically be stored under the compound 1,1,2-trimethylcyclohexane. You can check this by:

   i.   Clicking **Thermo Physical** on the **Menu Bar**
   ii.   Selecting **Databank** on the **Thermo Physical Menu**
   iii. Selecting **View/Edit** on the **Databank Menu**
   iv.   Selecting 1,1,2-trimethylcyclohexane from the component list

v.   Clicking on the **Vapor Pressure and the Data Button on the View/Edit Component Data Menu**

The following screen will appear:
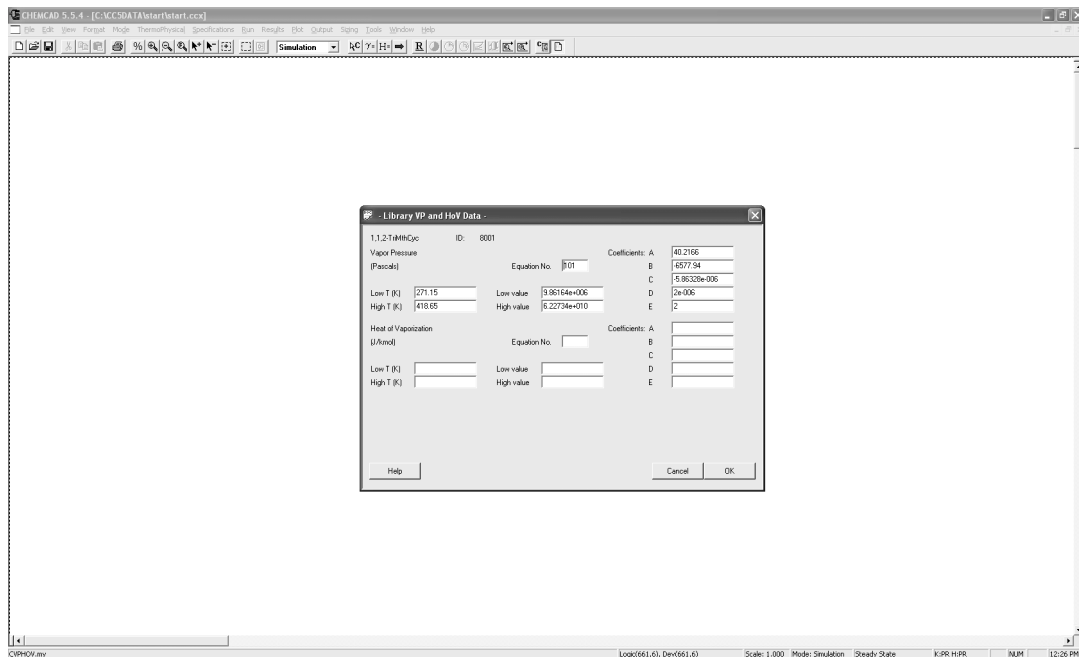
PHYSICAL PROPERTIES METHODS AND HIERARCHIES

Several of the temperature dependent transport properties can be calculated in multiple ways. Selection of K value model affects the calculation of some properties. Availability of data can influence selection of an estimation method, when equation parameters are not present.

This section explains the various calculation methods for transport properties, and the order in which CHEMCAD will attempt to select a method.

Vapor Pressure will always use the hierarchy described below. The default method for Ideal Gas Heat Capacity can be changed at the enthalpy dialog. Default method for the other transport properties can be changed by going to the **thermophysical** menu and selecting **transport properties**.
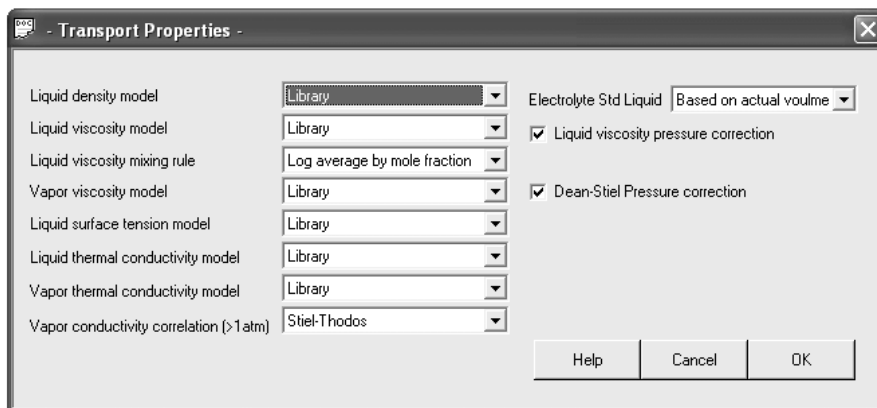
VAPOR PRESSURE

For equation of state K-value methods (SRK, PR), the vapor pressure is calculated by the equation of state. This calculation generally involves Tb, Tc, Pc, and the acentric factor.

For the Ideal Vapor Pressure and for the activity coefficient K-value methods, pure component vapor pressures are calculated. In CHEMCAD this is done in one of three ways:

i.   Using the DIPPR equation
ii. Using the Antoine equation
iii. Using the Curl-Pitzer method

In the default condition, the program will look first to the DIPPR equation. If the DIPPR coefficients are not present, then CHEMCAD will try to use the Antoine equation. If neither the DIPPR or the Antoine coefficients are available, the program will use the Curl-Pitzer Method which is based on critical properties.

THE DIPPR-VAPOR PRESSURE EQUATION:

$$\ln VP = A + \frac{B}{T} + C \ln T + DT^E$$

Note: alternate DIPPR equation forms are occasionally used for vapor pressure.

THE ANTOINE VAPOR PRESSURE EQUATION:

$$\ln VP = A + \frac{B}{T+C}$$

THE CURL-PITZER VAPOR PRESSURE EQUATION:

$$\ln P_{vpr} = f^{(0)} + \omega f^{(1)}$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 \, T_r^6$$

$$f^{(1)} = 15.218 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 \, T_r^6$$

where P_{vpr} =   reduced vapor pressure
             T_r =   reduced temperature
             ω =   acentric factor

LIQUID DENSITY OPTIONS

CHEMCAD will permit the user to select the liquid density method used during the simulation from one of four methods:

1. The DIPPR (Library) Equation
2. The API Method
3. The CAVETT Equation
4. The RACKETT Equation

The DIPPR method is the default. If the DIPPR method coefficients are not available in the databank, the program uses the API method. Since this method requires the specific gravity at 60°F, if the specific gravity (60/60) is not available, the Cavett equation is used.

Note that the default method for a simulation can be changed. Go to the **thermophysical** menu and select **transport properties** to change the default method.

1. **The DIPPR Equation**

   The DIPPR density equation has the following form:

   $$\text{Density} = A / \left(B^{\left[1 + (1 - T/C)^D \right]} \right)$$

   where   Density is in kgmoles/m^3
                  Temperature is in degrees Kelvin

       A, B, C, D are component specific coefficients stored in the databank (items 26 through 29)

       Note: alternate DIPPR equation forms are occasionally used for density.

2. **The API Method**

   The API method is based on Figure 6A2.21 and Procedure 6A2.21 and 6A2.22 of the API databook.

   The correlation is based on the relationship $C_1/d_1 = C_2/d_2$ = constant, where d_1 and d_2 represent two densities and C_1 and C_2 represent the corresponding density correlation factors.

   Where this relation holds, any density may be expressed as a function of one known density:

   $$d2 = d1 \, \frac{C_2}{C_1}$$

   where   d   =   the density in units of weight per volume, and

C = represents an empirical density correlation factor (explained below)
C = $A_{(0)} + A_{(1)} Tr + A_{(2)} Tr^2 + A_{(3)} Tr^3$

Each coefficient in the above equation is determined by:

$$A_{(i)} = B_{0(i)} + B_{1(i)} Pr + B_{2(i)} Pr^2 + B_{3(i)} Pr^3 + B_{4(i)} Pr^4$$

where Tr = reduced temperature
i = 0,1,2,3
P_r = reduced pressure

The coefficients are as follows:

i	$B_{0(i)}$	$B_{1(i)}$	$B_{2(i)}$	$B_{3(i)}$	$B_{4(i)}$
0	1.6368	-0.04615	$2.1138(10^{-3})$	$-0.7845(10^{-5})$	$-0.6923(10^{-6})$
1	-1.9693	-0.21874	$-8.0028(10^{-3})$	$-8.2328(10^{-5})$	$5.2604(10^{-6})$
2	2.4638	-0.36461	$-12.8763(10^{-3})$	$14.8059(10^{-5})$	$-8.6895(10^{-6})$
3	-1.5841	-0.25136	$-11.3805(10^{-3})$	$9.5672(10^{-5})$	$2.1812(10^{-6})$

C_1 is stored in the databank as the specific gravity at 60°F (item 42). D_1 equals d at 60°F. d_2 is then determined by evaluating C_2 and applying it to the above ratio.

The average error in estimating the density of a pure hydrocarbon is 1 percent. However, errors up to 10 percent can be expected at reduced temperatures greater than 0.95.

3. **The CAVETT Equation**

The Cavett equation has the form:

Liquid volume = Vol Con * (5.7 + 3Tr)

where Liquid volume is in cc/gmole
Vol Con is the liquid mole volume constant (item 9 in the databank)
Tr is the reduced temperature

4. **The Modified RACKETT equation**

The Modified RACKETT equation which was developed by Rackett and later modified by Spencer and Danner is used to estimate saturated volumes:

$$V = \frac{RTc}{Pc}(Z_{RA})[1 + (1 - Tr)]^{2/7}$$

Z_{RA} is a unique constant for each compound.

Liquid density can be selected from the Thermo/Transport Properties menu.

VAPOR VISCOSITY

The following methods are used by CHEMCAD for the calculation of vapor viscosity. The DIPPR method is the default.

1. DIPPR Library equation
2. Chapman-Enskog (for low pressure gases)

    a.   Neufield method for collision integral
    b.   Brokaw method for collision integral
3.   Method of Thodos

Note that the default method for a simulation can be changed. Go to the **thermophysical** menu and select **transport properties** to change the default method.

For low pressure gas, the Chapman-Enskog relation is used:

$$\mu_g = \frac{5/16\,(\pi\,MRT)^{0.5}}{(\pi\,O^2)\Omega_v} = 22.69\,\frac{(MT)^{0.5}}{O^2\,\Omega_v} = (M_p)\,P$$

where   M   =   molecular weight
            R   =   gas law constant
            T   =   temperature
            P   =   pressure
            O   =   molecular diameter
            Ω_v =   collision integral
            Mp   =   dipole moment

For non-polar gases the method of Neufeld is used to evaluate Ω_v:

$$\Omega_v = \frac{A}{T^{*\,B}} + \frac{C}{\exp D\,T^*} + \frac{E}{\exp F\,T^*}$$

where   T*   =   kT/e
            A   =   1.16145
            B   =   0.14874
            C   =   0.52487
            D   =   0.77320
            E   =   2.16178
            F   =   2.43787

For polar compounds Ω_v is evaluated using the method of Brokaw:

$$\Omega_v = \Omega_v\,(LJ) + \frac{0.2\,\delta^2}{T^*}$$

where Ω_v (LJ)   =   The Leonard-Jones collision integral
            δ =   The polar parameter
            T*   =   kT/e
            k   =   Boltman's constant
            e   =   The energy potential parameter

If c/k and d are unavailable in the database, an alternative method for evaluating gas viscosity is the method of Thodos:

For gases:

$$\mu = \frac{4.61\,Tr^{0.618} - 4.04\,e^{-0.449\,Tr} + 1.94\,e^{-4.058\,Tr} + 0.1}{\xi}$$

where   Tr   =   reduced temperature
        x   = $Tc^{0.166}\,M^{-0.5}\,Pc^{-0.67}$

Vapor Viscosity Mixing

The viscosities of gas mixtures are evaluated using the method of Wilke:

$$\mu_m = \sum_{i=1}^{n} \frac{y_i\,\mu_i}{\sum_{j=1}^{n} y_j\,\phi_{ij}}$$

$$\phi_{ij} = \frac{\left[1 + \left(\mu_i/\mu_j\right)^{0.5}\left(M_j/M_i\right)^{0.25}\right]^2}{\left[8\left(1 + M_i/M_j\right)\right]^{0.5}}$$

where m_i =   the pure component viscosity
        M_i =   the pure component molecular weight

The method of Dean and Stiel is used for the effect of pressure on the viscosity of gas mixtures.

LIQUID VISCOSITY

The following methods are used by CHEMCAD for the calculation of liquid viscosity. The default method is the DIPPR equation.

Note that the default method for a simulation can be changed. Go to the **thermophysical** menu and select **transport properties** to change the default method. You may also override the basis for the mixing rule.

1.   The DIPPR (Library) Equation
2.   The two-term liquid viscosity equation
3.   The Letsou Steil method

The ASME method is used for pseudocomponent estimations.

1.   The primary method for computing liquid viscosities of a pure component is the DIPPR library equation which has the following form:

$$\mu = \exp\left[A + B/T + C\,Ln\,T + D\,T^E\right]$$

where μ =   the liquid viscosity in Pascal seconds

A, B, C, D, =   DIPPR coefficients for liquid viscosities

E

Note: Alternate DIPPR equation forms are occasionally used for viscosity.

2. If the DIPPR data is absent, the following two-term equation is used:

$$\text{Log}\,\mu = A\left(1/T - 1/B\right)$$

where μ =   the liquid viscosity in centipoise

A and B   =   DIPPR coefficients stored in the databank (items 30 and 31)

3. If coefficients for methods 1 and 2 are not available, the method of Letsou and Steil is used.

$$\mu = \frac{(\mu\xi)^0 + \omega(\mu\xi)^{(1)}}{\xi}$$

$$\xi = \frac{T_c^{1/6}}{MW^{1/2}\,P_c^{2/3}}$$

where $(\mu\xi)^{(0)}$ = $0.015174 - 0.02135\,T_R + 0.0075\,T_R^2$

$(\mu\xi)^{(0)}$ = $0.042552 - 0.07674\,T_R + 0.0340\,T_R^2$

where T_c =   critical temperature

x   = $T_c^{0.166}\,M^{-0.5}\,P_c^{-0.67}$

MW   =   molecular weight

W   =   the acentric factor

4. For pseudo-components, CHEMCAD uses the method of ASME for liquid viscosity estimation.

Liquid Viscosity Mixing Rule
The following mixing rule is used for the liquid-mixture viscosities:

$$\text{Ln}\,(\mu) = \sum_i X_i\,\text{Ln}\,(\mu i)$$

The default mixing rule uses mol fraction for X_i. The user may override this mixing rule to use mass fraction for X_i. This is occasionally used for estimating the viscosity of a mixture with high MW polymers.

VAPOR THERMAL CONDUCTIVITY

The following methods are used by CHEMCAD for the calculation of vapor thermal conductivity. The default method is the DIPPR equation:

1. The DIPPR Library Equation
2. API Procedures for Liquid Viscosity

Note that the default method for a simulation can be changed. Go to the **thermophysical** menu and select **transport properties** to change the default method.

The DIPPR Equation

$$\lambda_V = \frac{A\,T^B}{1 + C/T + D/T^2}$$

where
- I_v = the gas thermal conductivity in w/m.K
- A, B, C and D = DIPPR coefficients
- T = temperature in Kelvin

The Stiel-Thodos method is used for high pressure correction.

For liquids

$$\lambda_L = A + BT + CT^2 + DT^3 + ET^4$$

where
- I_L = the liquid thermal conductivity in w/m.K
- A, B, C and D = DIPPR coefficients
- T = temperature in Kelvin

For gases where the DIPPR data is absent, CHEMCAD uses the API procedure (12B1.5) to estimate component thermal gas conductivities.

- API procedure 12B4.1 is used for high pressure correction, and API procedure 12B2.1 is used for mixing rules for gas mixtures.

For liquids where the DIPPR data is absent, the following methods are used:

- API procedure 12A1.2 for pressure < 500 psia and TR < 0.8
- API Figure 12A3.1 for hydrocarbon fractions
- API Figure 12A4.1 for high pressure correction
- API procedure 12A1.3 if the methods above do not apply
- API procedure 12A2.1 is used as the mixing rule

SURFACE TENSION FOR PURE COMPONENTS

For Surface Tension, CHEMCAD uses the Hakim equation, the Miller equation and the Hydrocarbon Correlation.

1. Hakim equation:

$$\sigma = Pc^{2/3}Tc^{1/3}Qp\left(\frac{1-Tr}{0.4}\right)$$

where,
- σ = Surface tension of polar liquid
- Pc = Critical pressure
- Tc   Critical temperature, K
- Qp = $0.1574 + 0.395w - 1.769x - 13.69x^2 - 0.510w^2 + 1.298wx$

m $=$ $1.210 + 0.5385w - 14.61x - 32.07x^2 - 1.656w^2 + 22.03wx$

x $=$ Stiel polar factor

w $=$ the acentric factor

2. Miller Equation:

$$\sigma = Pc^{2/3}Tc^{1/3}Q(1 - Tr)^{11/19}$$

$$Q = 0.1207\left(1 + \frac{Tb_r LnPc}{1 - Tb_r}\right) - 0.281$$

3. Hydrocarbon Correlation:

$$\sigma = 673.7\frac{\left[\dfrac{(Tc - T)}{Tc}\right]^{1.232}}{K} \tag{10A3.2-1}$$

where σ = Surface tension of polar liquid
         Tc = Critical temperature in Rankine
         T = Temperature of system in Rankine
         K = Watson characterization factor

DEFINING NEW COMPONENTS FROM DISTILLATION CURVES

A petroleum blend can be modeled as a mixture of components with various boiling points. These components are called pseudocomponents, as each represents a narrow boiling mixture of several components.

CHEMCAD has two options for creating components to model the properties of crude oil or any other material requiring an assay. These are:

*   Input the distillation curve and associated data defining the material; or
*   Select the crude from the CHEMCAD Crude Oil databank.

The crude oil databank information is given in the appendices to this manual. The distillation curve input procedure is described below.

DISTILLATION CURVE INPUT PROCEDURE

This option can be used to perform a petroleum assay analysis. A CHEMCAD simulation may obtain up to 10 assays, based on ASTM D86, ASTM D1160, D2887 TBP, 10mm TBP laboratory data, or TBP at any specified pressure. The standard laboratory analysis records the temperature and amount distilled of an initial 100 cc of crude stock.

At least five points of a volume versus temperature curve are required. However, more points are strongly recommended, especially those at the following volume percentages: 0, 5, 10, 30, 50, 70, 90, 95, and 100. The program will extrapolate the 0 and 100% points if they are not entered. A maximum of 36 points may be specified. When a light-ends analysis is given, it overrides the 0% volume temperature.

The gravity of an assay must be specified. The minimum information required is the bulk gravity. Also, a gravity curve, mid-volume % versus gravity, may be entered. A gravity curve must have a least two points, but more are recommended especially the curve endpoints. If you wish to enter both a gravity curve and a bulk gravity, the program will adjust the gravity curve to satisfy the bulk gravity condition.

If two or more streams are described by assays the user has the option of blending or not blending them. If blending is selected the Distillation Curve Characterization routine finds the temperature regions where the temperature versus volume curves overlap and calculates the average gravity of each cut in the common temperature regions. Blending prevents cases with too many pseudocomponents. The results consist of molar flow rates of the streams that are blended.

If "no blending" is selected, then each assay will be characterized individually and, therefore, will have its own set of pseudocomponent. The "no blending" option is inherently more accurate, but adds bulk to the simulation.

The Procedure:

1. First, define any pure compounds in the flowsheet. If the curve is going to be used in a problem where steam is used for distillation, then Water (62) must be in the component list. Other light hydrocarbons, the "light ends", are commonly present. You must also select these components.

2. Invoke the **Distillation Curve** command from the **Thermophysical Menu**. The first time you use the command, the program will display a screen prompting you for ID numbers of streams to be characterized.

3. Select which correlation to use for characterizing the distillation curve(s) and for estimating the pseudocomponent properties.

   Options:

Molecular Weight:	**Critical Properties**	**ASTM D86-TBP Interconverison Method**
Chemstations [Default]	Cavett [Default]	Chemstations [Default]
Old API	API	New API
New API	Lee Kesler	
Lee Kesler		

4. The next screen will ask you to enter the Temperature Cut range. The range of the cut and the number of cuts determine the "width" of a boiling range in each pseudocomponent. The default ranges will be shown in the input screen:

100 to 800 degrees F	28 cuts
800 to 1200 degrees F	8 cuts
1200 to 1600 degrees F	4 cuts

   For metric units, the default is the same with the temperatures converted to degrees C. Cuts may be explicitly specified in the three columns on the right-hand side of the second spreadsheet.

For example, the default range shows that there are 4 points in the range between 1200 and 1600 F. Meaning, each pseudocomponent in that range will be 100 degrees wide.

5. Select **Edit Curve Data** to enter the bulk properties for the whole material.

Curve Type	Input the type of distillation curve you are using. Options are: ASTM D86 (760 mmHg) ASTM D1160 (10 mmHg) True Boiling Point (760 mmHg) True Boiling Point (10 mmHg) D1160 at a specified pressure True Boiling Point at a specified pressure D2887 (Gas Chromatography)
Pressure	Enter the pressure for the options above that require a specified pressure.
Gravity Type	Choose the type of the bulk gravity. Select either specific gravity or API gravity.
Bulk Gravity	This value is not required if a gravity curve is to be entered. A value must be entered if you do not specify a gravity curve. If both a gravity curve and a bulk gravity are specified, the program will adjust the gravity curve until the calculated bulk gravity matches the specified bulk gravity. If water is present, the bulk gravity may be either on a wet or dry basis. If it is on a dry basis, the amount of water should be entered in the same units as the total flowrate. If it is on a wet basis, the percentage of water must be specified on the light ends dialog box.
Total Flow Units	Select flow units to use for the feed rate. Click the choice box to see the options: BPSD (Barrels per stream day) Barrels/hr M3/day M3/hour
Total Flow Rate	Enter the total flow rate in the units specified above.
Total Water	If all the data are on a dry basis, an arbitrary amount of water may be included here, in the same flow unit as the total flow.
Light-ends Flow	Click the choice box to see the options: Volume % Weight % Mole/hr Mass/hr
Distillation	Defines the units for the distillation curve.
Curve Unit	Click the choice box to see the options: Volume % Weight %

Blend / No Blend   Designate whether the program is to blend the curves and generate fewer components. If blending is not performed, each curve will be characterized by its own unique set of pseudocomponents and be more precise.
Options are:
Blend
No Blend

6. A dialog box is now displayed that allows you to enter the actual distillation curve. This dialog box has two columns for entering temperature versus volume percent and gravity versus volume percent data.

    Percents need not be entered in numerical order. The program will put them in order for you when you hit the **OK** button.

7. The next dialog box allows you to input a gravity curve for the whole curve. If you have entered a bulk gravity, then this data is optional. However, if you provide both the bulk gravity and a gravity curve, the program will adjust the gravity curve to match the bulk gravity.

8. Finally, the Light Ends Analysis dialog box appears. This dialog box is displayed only when water or light hydrocarbons are present in the feed.

9. Use the **Edit Curve Data Menu** to go back and change any data for the assay.

10. Click on **Save and Exit** to start calculations.

The program performs the following sequence of steps while executing the data:

a. For each assay, it converts data to a TBP curve.
b. It breaks each curve into cuts.
c. It determines the gravities of all the cuts.
d. It finds the average gravities of overlapping curves, if multiple assays are specified, and the "blending"option is selected.
e. It determines the molecular weight of the cuts.
f. It determines other physical properties and constants of cuts.
g. It stores the component properties and constants in a file which serves as a data base.
h. It calculates the molar flowrates and stores them in a file.
i. It displays the results in **WORDPAD**. From there it can be printed.

This report will be displayed in **WORDPAD**.

You may also plot this data by invoking the **Plot** command, then the **Distillation Curves** option.

If the Distillation Curve routine aborts or stops without completion, it is recommended that you plot the temperature versus volume curve on paper to see if it is realistic. Assays with over 40% light ends by volume may have to be split into two streams: one with just light ends and the other with the petroleum cuts.

METHODS USED TO CALCULATE THE PHYSICAL PROPERTIES OF DISTILLATION CURVE PSEUDO-COMPONENTS

MOLECULAR WEIGHT FOR DISTILLATION CURVE PSEUDOCOMPONENTS

The user can choose from four methods to calculate molecular weight using the pseudo-component method. These are:

The Chemstations Method
The Old API Method
The New API Method
The Lee-Kesler Method.

All four of these methods are described below:

THE CHEMSTATIONS METHOD FOR MW

$$MW = 0.5(MW2 + MW3)$$

where   MW2   =   the Molecular Weight as calculated by the old API Method.
         MW3   =   the Molecular Weight as calculated by the new API Method.

If the MW as calculated above is greater than 250;

$$MW = \rho(-11.985 + 2.4966 * \log T_b - 1.174 * \log SG$$

If the MW as calculated above is greater than 500;

$$MW = 0.5(W4 + MW3)$$

where, MW4 is the MW as calculated by the Lee-Kesler Method.

THE OLD API METHOD FOR DISTILLATION CURVE MW

$$MW = 204.38 * T_b^{0.118} * SG^{1.88} * \rho^{0.00218 * T_b} * \rho^{-3.07 * SG}$$

THE NEW API METHOD FOR DISTILLATION CURVE MW

$$MW = 20.486 * [\rho^{1.565\rho - 4 * T_b - 7.78712 * SG + 1.1582\rho - 3 * T_b * SG}] * T_b^{1.26} * SG^{4.983}$$

THE LEE-KESLER METHOD FOR DISTILLATION CURVE MW

$$MW = -12272.6 + 9486 * SG + (4.6523 - 3.3287 * SG) * T_b +$$
$$(1.0 - 0.77084 * SG - 0.02058 * SG^2] * \left(1.3437 - \frac{720.79}{T_b}\right) * \frac{187}{T_b} +$$
$$(1.0 - 0.80882 * SG + 0.0226 * SG^2)\left(1.8828 - \frac{181.98}{T_b}\right) * \frac{1.0\rho12}{T_b^3}$$

CRITICAL PROPERTIES FOR DISTILLATION CURVE PSEUDOCOMPONENTS

CAVETT METHOD FOR DISTILLATION CURVE CRITICAL PROPERTIES

If the **Cavett Method (default)** is chosen by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$Tc = 768.0712 + 1.7133693 * T_b - 0.0010834 * T_b^2 -$$
$$0.008921258 * T_b * API + (3.8890584 \, \rho\text{-}7) + T_b^3$$
$$5.309492 \, \rho\text{-}6 * T_b^2 * API + 3.27116 \, \rho\text{-}8 * (T_b * API)^2$$

$$\log Pc = 2.829046 + 0.0009412 * T_b - 3.047475 \, \rho\text{-}5 * T_b^2 -$$
$$2.087611 \, \rho\text{-}5 * API * T_b + 1.5184103 \, \rho\text{-}9 * T_b^3 +$$
$$1.1047809 \, \rho\text{-}8 * API * T_b^2 - 4.82716 \, \rho\text{-}8 * API^2 * T_b +$$
$$1.3949619 \, \rho\text{-}10 * (API * T_b)^2$$

$$Vc = \frac{Zc * Tc * 10.73}{Pc}$$

where   Tc   =   Critical temperature in R
            Pc   =   Critical pressure in psia
            Zc   =   Critical compressibity factor calculated like so:

$$Zc = \frac{1}{3.43 + 6.7 \, \rho\text{-}9 * \Delta^2}$$

and

$$\Delta = (8.75 + 1.987(\log T_b) + T_b) / 1.8 \ \text{ if } \ Tc \langle 536.67 \, R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by f:

$$f = \left(\frac{Tc - 536.67}{Tc - T_b} \right)^{0.38}$$

if Tc > 593 R:

$$\Delta = \left(\frac{(0398907 * \text{specific gravity}) \, (\Delta - 592.4439)}{MW} \right)^{0.5}$$

$$\Omega = \frac{-\log Pc - 5.92714 + 6.09648 / \theta + 1.28862 * \log \theta - 0.169347 \, \theta^6}{15.2518 - 15.6875 / \theta - 13.4721 * \log^\Theta + 0.43577 * \theta^6}$$

where   Pc   =   pressure in atm
          θ =   normal boiling point/critical temperature in R

The ideal gas heat capacity is calculated as follows:

α = $(0.036863384 * K - 0.4673722) * MW$
β = $(3.1865 \rho - 5 * K + 0.001045186) * MW$
γ = $-4.9572 \rho - 7 * MW$

and

$$Cp_g = \alpha + \beta * T + \gamma * T^2 \ \ in \ \ \frac{BTU}{lbmol\,R}$$

where Cp_g =   Ideal gas heat capacity
          T   =   System temperature in R

API METHOD FOR DISTILLATION CURVE CRITICAL PROPERTIES

If the **API Method** is selected by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$Tc = 24.2787 * T_b{}^{0.58848} * SG^{0.3596}$$

$$\ln Pc = \frac{3.12281\,\rho + 9}{T_b{}^{2.3125} * SG^{2.3201}} \ \text{if } T_b \langle 1000°F, \text{ otherwise}$$

$$\ln Pc = 8.3634 - \frac{0.566}{SG} - \left(0.24244 + \frac{2.2898}{SG}\right) + \left(\frac{0.11857}{SG^2}\right) * 0.001 * T_b$$

$$+ \left(1.4685 + \frac{3.648}{SG} + \left(\frac{0.47127}{SG^2}\right)\right) * I\,\rho - 7 * T_b{}^2 -$$

$$\left(0.42019 + \frac{1.6977}{SG^2}\right) I\rho - 10 * T_b{}^3$$

$$Vc = \frac{Zc * Tc * 10.73}{Pc}$$

where   Tc   =   critical temperature in R
          Pc   =   critical pressure in psia
          Zc   =   critical compressibility factor calculated like so;

$$Zc = \frac{1}{3.43 + 6.7\,\rho - 9 * \Delta^2}$$

and,

$$\Delta = \left(8.75 + 1.987(\log T_b) * T_b\right) / 1.8 \text{ if } Tc \langle 536.67\,R$$

if $536.67 < Tc < 593$ R, the above result for Δ is multiplied by, f;

$$f = \left(\frac{Tc - 536.67}{Tc - T_b} \right)^{0.38}$$

if Tc > 593 R,

$$\Delta = \left(\frac{(0.98907 * \text{specific gravity})(\Delta - 592.4439)}{MW} \right)^{0.5}$$

$$\Omega = \frac{-\log Pc - 5.92714 + 6.09648/\theta + 1.28862 * \log\theta - 0.169347\,\theta^6}{15.2518 - 15.6875/\theta - 13.4721 * \log^\theta + 0.43577 * \theta^6}$$

where   Pc   =   Critical pressure in atm
          θ =   Normal Boiling Point / Critical Temperature in R

The ideal gas heat capacity is calculated as follows:

α =   (0.036863384 * K – 0.4673722) * MW
β =   (3.18565 ρ - 5 * K + 0.001045186) * MW
γ =   -4.9572 ρ - 7 * MW

and

$$Cp_g = \alpha + \beta * T + \gamma * T^2 \text{ in } \frac{BTU}{\text{lbmol R}}$$

where Cp_g =   ideal gas heat capacity
          T   =   system temperature in R

LEE-KESLER METHOD FOR DISTILLATION CURVE CRITICAL PROPERTIES

If the **Lee-Kesler Method** is selected by the user, Tc, Pc, Vc, Ω and Cp_g are calculated as follows:

$$Tc = 341.7 + \frac{811}{SG} + (0.4244 + 0.1174\,SG) * T_b +$$

$$(0.4669 - 3.2623\,SG) * \frac{100,000}{T_b}$$

$$\ln Pc = 8.3634 - \frac{0.0566}{SG} - \left(0.24244 + \frac{2.2898}{SG} + \frac{0.11857}{SG^2} \right) *$$

$$0.00\ln T_b + \left(1.4685 + \frac{3.648}{SG} + \frac{0.47127}{SG^2} \right) * \mathsf{I}\,\rho - 7 * T_b{}^2 -$$

$$\left(0.42019 + \frac{1.6977}{SG^2} \right) * \mathsf{I}\,\rho - 10 * T_b{}^3$$

$$Vc = \frac{Zc * Tc * 10.73}{Pc}$$

where   Tc = critical temperature in R
         Pc = critical pressure in psia
         Zc = critical compressibility factor calculated like so:

$$Zc = \frac{1}{3.43 + 6.7\,\rho - 9 * \Delta^2}$$

and

$$\Delta = (8.75 + 1.987(\log T_b) * T_b)/1.8 \quad \text{if} \quad Tc \langle 536.67\,R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by, f;

$$f = \left(\frac{Tc - 536.67}{Tc - T_b}\right)^{0.38}$$

if Tc > 593 R,

$$\Delta = (8.75 + 1.987(\log T_b) * T_b)/1.8 \quad \text{if} \quad Tc \langle 536.67\,R$$

if 536.67 < Tc < 593 R, the above result for Δ is multiplied by, f;

$$f = \left(\frac{Tc - 536.67}{Tc - T_b}\right)^{0.38}$$

if Tc > 593 R,

$$\Delta = \left(\frac{(0.98907 * \text{specific gravity})(\Delta - 592.4439)}{MW}\right)^{0.5}$$

$$\Omega = \frac{-\log Pc - 5.92714 + 69648/\theta + 1.28862\,\rho\,\log\theta - 0.169347\,\theta^6}{15.2518 - 15.6875/\theta - 13.4721 * \log\theta + 0.43577 * \theta^6}$$

where   Pc   =   critical pressure in atm

         θ =   normal Boiling Point / Critical Temperature in R.

The ideal gas heat capacity is calculated as follows:

         α = $(0.036863384 * K - 0.4673722) * MW$
         β = $(3.1865\,\rho - 5 * K + 0.001045186) * MW$
         γ = $-4.9572\,\rho - 7 * MW$

and

$$Cpg = \alpha + \beta * T + \gamma T^2 \quad in \quad \frac{BTU}{lbmol\,R}$$

where Cp_g =   ideal gas heat capacity
            T   =   system temperature in R

DISTILLATION CURVE INTERCONVERSION

Distillation curve assays may be carried out under different conditions. CHEMCAD is able to convert results from the more common distillation curve methods to TBP, which is used for creating the pseudocomponents. The following methods are used for conversion of distillation curves.

INTERCONVERSION OF ASTM D86-TBP DISTILLATION CURVES AT ATMOSPHERIC PRESSURE

The following equations are used to interconvert ASTM D86 and atmospheric TBP distillation data.

$$TBP = a(ASTM\ D86)^b$$

$$ASTM\ D86 = a^{(-1/b)}\ (TBP)^{(1/b)}$$

where   a, b   =   constants varying with percent of liquid sample distilled as given below:

Volume % distilled	a	b
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110
95	0.8008	1.0355

TBP   =   true boiling point temperatures at 0, 10, 30, 50, 70, 90, and 95 volume percent distilled, in degrees Rankine.

ASTM D86   =   observed ASTM D86 temperatures at corresponding volume percent distilled, in degrees Rankine.

LIMITATIONS

This procedure should not be used outside the following temperature ranges:

Volume % Distilled	ASTM D86 Temperature Range, F	TBP Temperature Range, F
0	73-599	-50-616
10	97-583	51-561
30	119-596	97-590
50	138-608	135-608
70	151-621	153-626

90	166-647	181-662
95	162-750	163-794

RELIABILITY

Differences between the estimated and experimental TBP and ASTM D86 temperatures are as given below at various volume percent distilled points.

Volume % Distilled	Average Deviation, F
0	21.
10	11.1
30	7.6
50	6.1
70	6.6
90	7.9
95	11.

Deviations are valid when starting with either an ASTM or TBP distillation and converting to the other. Seventy-eight sets of data were used in developing this procedure over the entire range of applicability.

INTERCONVERSION OF D1160 – TBP 10 mm Hg DISTILLATION CURVES

Figure 3A2.1 from the API Technical Databook relates ASTM D1160 and TBP distillation data at 10 mm Hg absolute pressure. The ASTM D1160 and TBP 50 percent points at 10 mm Hg are assumed to be equal.

EXAMPLE

Estimate the TBP curve at 10 mm Hg for a petroleum fraction having the following ASTM D1160 distillation temperature at 10mmHg.

Volume percent distilled	10	30	50	70	90
ASTM D1160 temperature, F	300	400	475	550	650

First, from Figure 3A2.1, find the temperature differences for each segment of the TBP curve at 10 mm Hg.

Segment of Curve (Volume Percent)	10 mm Hg ASTM D1160 Temperature Difference (Degrees Fahrenheit)	10 mm Hg TBP Temperature Difference (from Fig. 3A2.1) (Degrees Fahrenheit)
10 to 30	100	106
30 to 50	75	82
50 to 70	75	75
70 to 90	100	100

The TBP temperatures are then calculated.   The ASTM D1160 and TBP distillation 50-percent temperatures are assumed to be equal at 10 mm Hg absolute pressure.   Here, the 50-percent temperature is 475 F:

10-percent temperature = 393 – 106 = 287 F   70-percent temperature = 475 + 75 = 550 F
30-percent temperature = 475 – 82 = 393 F   90-percent temperature = 550 + 100 = 650 F

CONVERSION OF SIMULATED DISTILLATION (ASTM D2887) TO ASTM D86 DISTILLATION

The following equation is used to convert a simulated distillation (SD) in weight percent to an ASTM D86 distillation in volume percent.

$$\text{ASTM D86} = a(SD)^b \, F^c$$

where   a, b, c   =   constants varying with percent of liquid sample distilled as given below.

% Distilled	a	B	c
0	6.0154	0.7445	0.2879
10	4.2262	0.7944	0.2671
30	4.8882	0.7719	0.3450
50	24.1357	0.5425	0.7132
70	1.0835	0.9867	0.0486
90	1.0956	0.9834	0.0354
100	1.9073	0.9007	0.0625

ASTM   D86   =   observed ASTM D86 temperatures at 0-, 10-, 30-, 50-, 70-, 90-, and 100-volume percent points, in degrees Rankine.

      SD   =   Simulated distillation temperatures at corresponding weight percent points, in degrees Rankine.

      F   =   0.009524(SD 10%)0.05434 (SD 50%)0.6147

LIMITATIONS

The procedure cannot be used reversibly to predict a SD distillation from an ASTM D86 distillation. Also this procedure should not be used outside the temperature ranges specified below:

Weight % Distilled	Simulated Distillation Temperature Range, F
0	-50-390
10	74-442
30	93-493
50	131-545
70	147-581
90	179-655
100	207-762

RELIABILITY

Differences between the estimated and experimental ASTM D86 temperatures at various points are given below. Data sets for 117 fractions were used to evaluate the accuracy of the procedure.

Volume % Distilled	Average Deviation, F
0	22.5
10	9.2
30	7.6
50	7.1
70	6.1
90	8.4
100	18.8

In addition, an evaluation of the two-step SD-ASTM-TBP method was made. Differences between the estimated and experimental TBP temperatures at various percent points are given below. Data sets for nine fractions were used to evaluate the accuracy of the procedure.

Volume % Distilled	Average Deviation, F
10	8.2
30	9.9
50	9.2
70	8.8
90	10.8

LITERATURE SOURCE

This procedure was developed by M.R. Riazi, The Pennsylvania State University, University Park, PA., private communication (1985).

INTERCONVERSION OF DISTILLATION DATA FOR PETROLEUM FRACTIONS AT SUBATMOSPHERIC PRESSURES

DISCUSSION

The following procedure is used to convert ASTM or TBP distillation data between subatmospheric pressures and between subatmospheric pressures and atmospheric pressure (760 mm Hg).

PROCEDURE

A. Data at Subatmospheric Pressure

    Step 1: Assume the Watson K of the petroleum fraction is 12, and convert the data using Procedure 5A1.13 below.

    Step 2: Since the Watson K is set at 12, no Watson K correction is necessary.

B. Data at Atmospheric Pressure

    Step 1: If the specific gravity and mean average boiling point are known or can be calculated, determine the Watson K from the defining equation. Otherwise assume K = 12.

    Step 2: Follow Procedure 5A1.13 below.

PROCEDURE 5A1.13:

    Step 1: Obtain the normal boiling point of the hydrocarbon and the Watson K.

    Step 2: Calculate a vapor pressure using $t_b = t_b'$, where t_b is equal to the normal boiling point and t_b' is the normal boiling point corrected to K = 12.

$$\log p^* = \frac{3000.538\, X - 6.761560}{43\, X - 0.987672} \text{ for } X > 0.0022 \left(p^* < 2\, \text{mm Hg}\right)$$

$$\log p^* = \frac{2663.129\ X - 5.994296}{95.76\ X - 0.972546} \text{ for } 0.0013 \leq X \leq 0.0022 \left(2\, \text{mm Hg} \leq p^* \leq 760\, \text{mm Hg}\right)$$

$$\log p^* = \frac{2770.085 \ X - 6.412631}{36 \ X - 0.989679} \text{ for } X < 0.0013 \left(p^* > 760 \text{ mm Hg}\right)$$

where

$$p^* = \text{vapor pressure, in mm Hg.}$$

$$X = \frac{\dfrac{T_b^{'}}{T} - 0.0002867 \left(T_b^{'}\right)}{748.1 - 0.2145 \left(T_b^{'}\right)}$$

where $T_b^{'}$ = normal boiling point corrected to K = 12, in degrees Rankine

$\quad\quad$ T = absolute temperature, in degrees Rankine

Step:3 Using the vapor pressure from Step 2, obtain a K-correction from the ΔT equation shown below. Subtract this ΔT (corrected with f multiplier for superatmospheric pressures) from the true normal boiling point to get the corrected normal boiling point, $T_b^{'}$.

$$\Delta T = T_b - T_b^{'} = 2.5 f \left(K - 12\right) \log \frac{p^*}{14.7}$$

where $\quad$ Tb $\quad$ = $\quad$ Normal boiling point, in degrees Rankine

$\quad\quad\quad$ f $\quad$ = $\quad$ Correction factor. For all subatmospheric vapor pressures and for all substances having normal boiling points greater than 400 F, f = 1. For substances having normal boiling points less than 200 F, f = 0. For superatmospheric vapor pressures of substances having normal boiling points between 200 F and 400 F, f is given by:

$$f = \frac{T_b - 659.7}{200}$$

$\quad\quad$ K $\quad$ = $\quad$ Watson characterization factor

Step 4: Repeat Steps 2 and 3 until the pressure used to estimate the K-correction in Step 3 agrees within desired limits with the value predicted in Step 2. In each repetition, the $t_b^{'}$ from Step 3 is used in Step 2.

MIXTURE PROPERTIES

VISCOSITY MIXING RULES

For **vapor mixtures**, the viscosity is calculated as shown:

$$\mu_m = \Sigma \frac{y_i\,\mu_i}{\Sigma\, y\, \phi_{ij}}$$

where μ_m =   mixture viscosity

             y_i =   vapor mole fraction

             μ_i =   pure component vapor viscosity

and

$$\phi_{ij} = \frac{\left[1 + \left(\dfrac{\mu_i}{\mu}\right)^{\frac{1}{2}}\left(\dfrac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2}{\left[8\left(1 + \dfrac{M_i}{M_j}\right)\right]^{\frac{1}{2}}}$$

where   M   =   molecular weight

For **liquid mixtures**, the viscosity is calculated as shown:

- If the molecular weight of any component in the mixture is greater than 2000, then:

$$A = \Sigma\left(\frac{x_i M_i}{M_T} * \ln\mu_i\right)$$

$$\mu_m = e^A$$

where M_T =   Molecular weight of the mixture

- If the molecular weight of components in the mixture are all less than 2000, then:

$$A = \Sigma\left(x_i \ln\mu_i\right)$$

$$\mu_m = e^A$$

- The user may specify to use mol fraction or mass fraction in this equation. By default, mol fraction is used.

THERMAL CONDUCTIVITY MIXING RULES

For **vapor mixtures** the thermal conductivity is calculated as shown:

$$k_m = \sum_{i=1}^{n} \frac{k_j}{\dfrac{1}{y_i} \displaystyle\sum_{j=1}^{n} A_{ij}\, y_j}$$

where   km   =   thermal conductivity of the mixture, in Btu per (hr) (sq.ft.) (deg. F) per ft
            ki   =   thermal conductivity of component i, in Btu per (hr) (sq.ft.) (deg. F) per ft
            n   =   number of components in the mixture
            yi, yj   =   Mole fractions of components i and j

$$A_{ij} = \frac{1}{4}\left\{1 + \left[\frac{\mu_i}{\mu_j}\left(\frac{M_j}{M_i}\right)^{\frac{3}{4}}\frac{\left(1+\dfrac{S_i}{T}\right)}{\left(1+\dfrac{S_j}{T}\right)}\right]^{1/2}\right\}^2 \frac{\left(1+\dfrac{S_{ij}}{T}\right)}{\left(1+\dfrac{S_i}{T}\right)}$$

$$S_i, S_j \ (\text{Sutherland Constants}) = 1.5\,T_b$$

$$S_{ij} = \sqrt{S_i S_j}$$

Note that $A_{ij} \neq A_{ji}$.

where μ_i, μ_j =   viscosities of components i and j, in centipoise
            M_i, M_j =   molecular weights of components i and j
            T_b =   normal boiling point, in degrees Rankine
            T   =   temperature, in degrees Rankine

This procedure yields average errors of approximately 2 percent and maximum errors of 15 percent when compared with the available data.

For **liquid mixtures** the thermal conductivity is calculated as shown below:

$$k_m = \sum_i \sum_j \phi_i\, \phi_j\, k_{ij}$$

$$k_{ij} = 2\left(\frac{1}{k_i} + \frac{1}{k_j}\right)^{-1}$$

where $K_{ij} = k_{ji}$ and $k_{ii} = k_i$

$$\phi_i = \frac{x_i V_i}{\sum\limits_j x_j V_j}$$

$$\sum_i \phi_i = 1$$

where k_m =   thermal conductivity of the mixture, in Btu per (hr) (sq.ft.) (deg. F) per ft
            ϕ_i, ϕ_j =   volume fractions of pure components i and j
            k_i, k_j =   thermal conductivities of pure components i and j, in Btu per (hr) (sq.ft.) (deg. F) per ft

V_i, V_j =   molar volumes of pure components i and j, in cu ft per lb-mole

x_i, x_j =   mole fractions of pure components i and j

Average deviations of values calculated by this procedure from experimental data are approximately 1 percent. Errors will rarely exceed 5 percent for hydrocarbon systems for which reliable pure-component input conductivities are available.

SURFACE TENSION MIXING RULES

The surface tension of mixture is calculated using the following expression:

$$\sigma_m^{1/4} = \rho_{L_m} \sum_{i=1}^{n} x_i \sigma_i^{1/4} / \rho_{L_i}$$

where σ_m =   mixture surface tension

σ_i =   pure component surface tension

ρ_{L_m} =   liquid density of the mixture

ρ_{L_i} =   pure component liquid density

x_i =   liquid mole fraction

REFERENCES

1. Benson, S. W., "Thermochemical Kinetics," Chap. 2, John Wiley & Sons, New York, 1968.

2. Bondi, A., Estimation of Heat Capacity of Liquids, Ind. Eng. Chem. Fundam., Vol. 5, No. 4, p. 442, November 1966.

3. Constantinou, L., and R. Gani, "New Group Contribution Method for Estimating Properties of Pure Compounds," AIChE J., 40 (10), p. 1,697 (1994).

4. "CRC Handbook of Chemistry and Physics," D. Lide, ed., CRC Press, Boca Raton, FL (1994).

5. Daubert, T. E., R. P. Danner, H. M. Sibul, and C. C. Stebbins, "Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation," Design Institute for Physical Property Data (DIPPR).

6. Joback K. G., and R. C. Reid, "Estimation of Pure-Component Properties from Group-Contributions," Chem. Eng. Commun., 57, p. 233 (1987).

7. Lee, B. I., and Kesler, M. G., A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States, AIChE J., Vol. 21, No. 3, p. 510, May 1975.

8. Letsou, A., and Stiel, L., Viscosity of Saturated Nonpolar Liquids at Elevated Pressures, AIChE J., Vol. 19, No. 2, p. 409, March 1973.

9. Lydersen, A. L., Estimation of Critical Properties of Organic Compounds, Report No. 3, U. of Wisconsin, College of Eng., Experimental Station, Madison, Wis., April 1955.

10. Misic, D., and Thodos, G., Atmospheric Thermal Conductivity for Gases of Simple Molecular Structure, J. Chem. Eng. Data, Vol. 8, No. 4, p. 540, October 1963.

11. Misic, D., and Thodos, G., The Thermal Conductivity of Hydrocarbon Gases at Normal Pressures, AIChE J., Vol. 7, No. 2, p. 264, June 1961.

12. Pitzer, K. S., others, Volumetric and Thermodynamic Properties of Fluids: II: Compressibility Factor, Vapor Pressure and Entropy of Vaporization, J. Amer. Chem. Soc., Vol. 77, p. 3433, July 5, 1955.

13. Reid R. C., J. M. Prausnitz, and B. E. Poling, "The Properties of Gases and Liquids," 4th ed., McGraw Hill, New York (1987).

14. Riedel, L., Neue Wärmeleitfähigkeitsmessungen and Organischen Flüssigkeiten, Chem. Ing. Tech., Vol. 23, No. 13, p. 321, January 1951.

15. Roy, D., and Thodos, G., Thermal Conductivity of Gases, Ind. Eng. Chem. Fundam., Vol. 7, No.4, p. 529, November 1968.

16. Roy, D., and Thodos, G., Thermal Conductivity of Gases, Ind. Eng. Chem. Fundam., Vol. 9, No. 1, p. 71, February 1970.

17. Spencer, C. F., and Daubert, T. E., Critical Evaluation of Methods for the Prediction of Critical Properties of Hydrocarbons, AIChE J., Vol. 19, No. 3, p. 482, May 1973.

18. Stiel, L., and Thodos, G., The Viscosity of Polar Gases at Normal Pressures, AIChE J., Vol. 8, No. 2, p. 229, May 1962.

19. Yoon, P., and Thodos, G., Viscosity of Nonpolar Gaseous Mixtures at Normal Pressures, AIChE J., Vol. 16, No. 2, p. 300, March 1970.

APPENDIX I   CRUDE OIL DATABANK

About the Crude Databank

A databank of several crude oil assays is maintained in CHEMCAD. The databank contains sufficient data to create petroleum fraction pseudo-components using the distillation curve method for creating new components.

List of Crudes for Distillation Curve Method

Crude Name	Country of Origin	Year of Assay	API Gravity	% Wt. Sulfur	Reid Vapor Pressure (psia)
BRENT BLEND	-	1995	38.3	0.4	8.5
EKOFISK	-	1989	39.2	0.169	2.83
DRIFT RIVER	-	1985	35.3	0.09	7.5
NEW MEXICO MIXED LIGH	-	1979	43.3	0.07	4.9
NIKISKI TERMINAL	-	1985	34.6	0.1	7.85
ABU MUBARRAS	ABU DHABI (U.A.E.)	1976	38.1	0.93	ND
EL BUNDUQ	ABU DHABI (U.A.E.)	1976	38.5	1.12	7
ABU AL BU KHOOSH	ABU DHABI, U.A.E.	1978	31.6	2	3.5
MURBAN	ABU DHABI, U.A.E.	1983	40.45	0.78	3.46
UMM SHAIF (ABU DHABI	ABU DHABI, U.A.E.	1983	37.4	1.51	7.05
ZAKUM (LOWER)	ABU DHABI, U.A.E.	1983	40.6	1.05	8.37
ZAKUM (UPPER)	ABU DHABI, U.A.E.	1981	33.1	2	ND
SAHARAN BLEND (43.7 A)	ALGERIA	1983	43.7	0.09	8.1
SAHARAN BLEND (45.5 A)	ALGERIA	1983	45.5	0.053	8.7
ZARZAITINE	ALGERIA	1983	43	0.07	6.6
CABINDA	ANGOLA	1983	31.7	0.17	3.8
PALANCA	ANGOLA	1985	40.14	0.11	ND
TAKULA	ANGOLA	1983	32.4	0.085	ND
JABIRU	AUSTRALIA	1989	42.3	0.05	2
GIPPSLAND	AUSTRALIA	1993	47	0.09	5.1
CHALLIS	AUSTRALIA	1989	39.5	0.07	3.4
SKUA	AUSTRALIA	1993	41.9	0.06	5.45
COOPER BASIN	AUSTRALIA	1991	45.2	0.02	5.3
GRIFFIN	AUSTRALIA	1991	55	0.03	5.4
SALADIN	AUSTRALIA	1990	48.2	0.02	4.7
NORTHWEST SHELF CONDENSATE	AUSTRALIA	1988	53	0.01	9.7
AIRLIE	AUSTRALIA	1988	44.7	0.01	4.4
BARROW ISLAND	AUSTRALIA	1988	37.3	0.05	4.6
JACKSON	AUSTRALIA	1987	43.8	0.03	1.25
HARRIET	AUSTRALIA	1987	37.9	0.05	3.55
BENIN	BENIN	1983	22.7	0.38	ND
GAROUPA	BRAZIL	1980	30	0.68	ND
SERGIPANO PLATFORMA	BRAZIL	1980	38.4	0.19	4.53
SERGIPANO TERRA	BRAZIL	1980	24.1	0.41	3.32

CHAMPION EXPORT	BRUNEI	1983	23.9	0.12	ND
SERIA	BRUNEI	1986	40.5	0.0627	4.3
SOVIET EXPORT BLEND	C.I.S.	1984	31.8	1.53	ND
KOLE MARINE	CAMEROON	1985	32.57	0.33	ND
LOKELE	CAMEROON	1984	20.73	0.46	1.45
CANADIAN SWEET	CANADA	1993	37.7	0.42	6.8
CANADIAN SOUR	CANADA	1993	37.5	0.56	8.6
BOW RIVER HEAVY	CANADA (ALBERTA)	1983	26.7	2.1	4.9
COLD LAKE	CANADA (ALBERTA)	1983	13.2	4.11	ND
FEDERATED PIPELINE	CANADA (ALBERTA)	1983	39.7	0.201	7.5
GULF ALBERTA	CANADA (ALBERTA)	1983	35.1	0.98	ND
LLOYDMINSTER BLENDED	CANADA (ALBERTA)	1983	20.7	3.15	ND
RAINBOW	CANADA (ALBERTA)	1983	40.7	0.5	ND
RANGELAND SOUTH	CANADA (ALBERTA)	1983	39.5	0.752	ND
WAINWRIGHT-KINSELLA	CANADA (ALBERTA)	1983	23.1	2.58	ND
PEMBINA	CANADA (ALBERTA)	1992	38.8	0.2	7.5
COLD LAKE BLEND	CANADA (ALBERTA)	1992	22.6	3.6	ND
SYNTHETIC CRUDE	CANADA (ALBERTA)	1991	38.7	0.19	ND
SYNTHETIC OSA STREAM (SUNCOR)	CANADA (ALBERTA)	ND	33.17	0.328	4.8
SHENGLI	CHINA	1983	24.2	1	ND
DAQUING (TACHING)	CHINA	1984	32.6	0.09	1.85
NANHAI LIGHT	CHINA	1992	40.58	0.059	5.45
WEIZHOU	CHINA	1986	39.7	0.08	ND
CANO LIMON	COLOMBIA	1989	29.3	0.51	0.7
DJENO BLEND	CONGO (BRAZZAVILLE)	1983	27.58	0.23	ND
EMERAUDE	CONGO (BRAZZAVILLE)	1973	23.6	0.6	3.1
MOSLAVINA	CROATIA	ND	37.35	0.4	8.5
SLAVONIJA	CROATIA	ND	30.9	0.4	8.5
PLINSKI KONDENZAT	CROATIA	ND	48.82	0.02	8.5
MARGHAM LIGHT	DUBAI (U.A.E.)	1985	50.33	0.04	9.8
FATEH	DUBAI, U.A.E.	1983	31.05	2	5.4
ORIENTE	ECUADOR	1989	29.2	0.88	2.2
BELAYIM	EGYPT	1983	27.5	2.2	6.5
GULF OF SUEZ	EGYPT	1983	31.9	1.52	8.3
RAS GHARIB	EGYPT	1977	21.5	3.64	ND
EAST ZEIT MIX	EGYPT	1992	39	0.89	ND
GAMBA	GABON	1984	31.43	0.09	ND
LUCINA MARINE	GABON	1975	39.6	0.05	ND
MANDJI BLEND	GABON	1983	30.1	1.11	ND
RABI-KOUNGA	GABON	1990	33.5	0.07	3.5
SALT POND	GHANA	1983	37.4	0.097	ND
BOMBAY HIGH	INDIA	1982	39.2	0.15	5.1
ARDJUNA	INDONESIA	1982	35.2	0.105	5.3
ATTAKA	INDONESIA	1982	43.3	0.04	6.89
BEKAPAI	INDONESIA	1983	41.2	0.08	3.9
CINTA	INDONESIA	1985	33.4	0.08	ND
DURI (SUMATRAN HEAVY)	INDONESIA	1989	21.3	0.18	0.44
MINAS (SUMATRAN LIGHT)	INDONESIA	1983	34.5	0.081	1.3

UDANG	INDONESIA	1983	38	0.05	ND
WALIO EXPORT MIX	INDONESIA	1983	35.4	0.68	2.4
BELIDA	INDONESIA	1991	45.1	0.02	ND
KAKAP	INDONESIA	1990	51.5	0.05	5.3
BADAK	INDONESIA	1993	49.5	0.032	6.3
ANOA	INDONESIA	1990	45.2	0.04	2.9
KATAPA	INDONESIA	#N/A	50.8	0.06	7.4
BIMA	INDONESIA	1987	21.1	0.25	1.1
WIDURI	INDONESIA	1990	33.25	0.07	< 0.5
ARUN CONDENSATE	INDONESIA	1980	54.8	0.018	11.6
IKAN PARI	INDONESIA	1990	48	0.02	6.6
LALANG (MALACCA STRAITS)	INDONESIA	1983	39.7	0.05	ND
ABOOZAR (ARDESHIR)	IRAN	1977	26.9	2.48	5.5
BAHRGANSAR/NOWRUZ	IRAN	1976	27.1	2.45	8
DORROOD (DARIUS)	IRAN	1983	33.6	2.35	6.5
FOROOZAN (FEREIDOON)	IRAN	1983	31.3	2.5	5.7
IRANIAN HEAVY	IRAN	1983	30.9	1.73	6.6
IRANIAN LIGHT	IRAN	1983	33.8	1.35	6.5
ROSTAM	IRAN	1976	35.9	1.55	ND
SALMON (SASSAN)	IRAN	1976	33.9	1.91	4.5
SOROOSH (CYRUS)	IRAN	1983	18.1	3.3	0.3
BASRAH HEAVY	IRAQ	1983	24.7	3.5	3
BASRAH LIGHT	IRAQ	1983	33.7	1.95	ND
BASRAH MEDIUM	IRAQ	1983	31.1	2.58	ND
KIRKUK BLEND	IRAQ	1983	35.1	1.97	5
NORTH RUMAILA	IRAQ	1976	33.7	1.98	ND
ESPOIR	IVORY COAST	1983	32.25	0.34	6.3
KUMKOL	KAZAKHSTAN	1993	42.5	0.07	ND
KUWAIT EXPORT	KUWAIT	1983	31.4	2.52	6.7
AMNA	LIBYA	1983	36	0.15	3.9
BREGA	LIBYA	1976	40.4	0.21	6.4
BU ATTIFEL	LIBYA	1982	43.3	0.04	2.1
ES SIDER	LIBYA	1983	37	0.45	4.8
SARIR	LIBYA	1983	38.4	0.16	5
SIRTICA	LIBYA	1982	41.3	0.45	10.4
ZUEITINA	LIBYA	1976	41.3	0.28	4.6
BURI	LIBYA	#N/A	26.24	1.76	ND
GRAND ISLE	LOUISIANA, USA	1975	34.2	0.35	1.6
BINTULU	MALAYSIA	1984	28.1	0.08	ND
LABUAN	MALAYSIA	1983	32.2	0.07	3.4
MIRI LIGHT	MALAYSIA	1983	32.6	0.04	4.7
TAPIS BLEND	MALAYSIA	1989	45.9	0.03	5.83
TEMBUNGO	MALAYSIA	1976	37.4	0.04	2.8
DULANG	MALAYSIA	1991	39	0.12	ND
ISTHMUS	MEXICO	1991	33.3	1.492	4.5
MAYA	MEXICO	1991	22.2	3.3	ND
OLMECA	MEXICO	1991	39.8	0.8	ND
BAXTERVILLE	MISSISSIPPI, USA	1982	16.3	3.02	ND

BURGAN	NEUTRAL ZONE	1983	23.3	3.37	3.4
EOCENE	NEUTRAL ZONE	1983	18.6	4.55	1.1
HOUT	NEUTRAL ZONE	1983	32.8	1.91	4.6
KHAFJI	NEUTRAL ZONE	1983	28.5	2.85	7.6
RATAWI	NEUTRAL ZONE	1976	23.5	4.07	3
BONNY LIGHT	NIGERIA	1993	33.92	0.135	ND
BONNY MEDIUM	NIGERIA	1983	25.2	0.23	3.1
BRASS RIVER	NIGERIA	1983	42.8	0.06	6.9
ESCRAVOS	NIGERIA	1983	36.4	0.12	4
FORCADOS	NIGERIA	1989	29.6	0.18	3.8
PENNINGTON	NIGERIA	1983	36.6	0.07	5.1
QUA IBOE	NIGERIA	1983	35.8	0.12	6
ANTAN	NIGERIA	1990	32.1	0.32	3.4
ARGYLL	NORTH SEA	1983	38	0.18	ND
AUK	NORTH SEA	1979	37.15	0.45	ND
BEATRICE	NORTH SEA	1983	38.7	0.05	5.6
BERYL	NORTH SEA	1983	37.5	0.32	5.2
BRAE	NORTH SEA	1983	33.6	0.73	ND
BUCHAN	NORTH SEA	1982	33.7	0.84	ND
CELTIC SEA	NORTH SEA	1983	44.3	0.06	ND
CORMORANT NORTH	NORTH SEA	1983	34.9	0.71	ND
CORMORANT SOUTH	NORTH SEA	1983	35.7	0.56	ND
DAN	NORTH SEA	1983	30.4	0.34	ND
DUNLIN	NORTH SEA	1979	34.9	0.39	ND
FLOTTA BLEND	NORTH SEA	1991	34.7	1.01	8.4
FULMAR	NORTH SEA	1983	39.3	0.26	ND
GORM	NORTH SEA	1983	33.9	0.23	ND
GULLFAKS	NORTH SEA	1990	29.3	0.44	ND
HUTTON	NORTH SEA	1978	30.5	0.65	ND
MAGNUS	NORTH SEA	1978	39.3	0.28	ND
MAUREEN	NORTH SEA	1978	35.55	0.55	ND
MONTROSE	NORTH SEA	1983	39.9	0.19	4
MURCHISON	NORTH SEA	1983	38	0.27	9
NINIAN BLEND	NORTH SEA	1982	35.8	0.43	5.4
PIPER	NORTH SEA	1979	35	1.04	ND
STATFJORD	NORTH SEA	1990	37.8	0.28	5.5
TARTAN	NORTH SEA	1983	41.7	0.56	10.2
THISTLE	NORTH SEA	1983	37.03	0.31	7.5
DANISH NORTH SEA	NORTH SEA (DENMARK)	1994	34.5	0.26	ND
OSEBERG	NORTH SEA (NORWAY)	1988	33.71	0.31	ND
EMERALD	NORTH SEA (NORWAY)	1991	22	0.75	0.6
FORTIES BLEND	NORTH SEA (UK)	1994	40.5	0.35	ND
DUNCAN	NORTH SEA (UK)	1983	38.49	0.18	ND
ALBA	NORTH SEA (UK)	1991	20	1.33	< 0.1
KITTIWAKE	NORTH SEA (UK)	1990	37	0.65	ND
INNES	NORTH SEA (UK)	1984	45.67	0.13	ND
ALIF	NORTH YEMEN	1987	40.3	0.1	6.59
OMAN EXPORT	OMAN	1984	34.7	0.94	4.5

KUBUTU	PAPUA NEW GUINEA	1992	44	0.04	ND
LORETO PERUVIAN EXPORT GR	PERU	1978	33.1	0.23	2.1
DUKHAN (QATAR LAND)	QATAR	1984	40.87	1.27	8.6
QATAR MARINE	QATAR	1984	36	1.42	5.3
RAS AL KHAIMAN	RAS AL KHAIMAN (U.A.E.)	1984	44.3	0.147	ND
SIBERIAN LIGHT	RUSSIA	1993	37.8	0.42	ND
ARAB LIGHT	SAUDI ARABIA	1991	33.4	1.77	3.6
ARAB EXTRA LIGHT (BERI)	SAUDI ARABIA	1992	37.2	1.15	4
ARAB MEDIUM (KHURSANIYAH)	SAUDI ARABIA	1992	28.5	2.85	3.2
ARAB MEDIUM (ZULUF/MARJAN)	SAUDI ARABIA	1992	28.8	2.49	4.8
ARAB HEAVY (SAFANIYA)	SAUDI ARABIA	1991	27.4	2.8	7.5
SHARJAH CONDENSATE	SHARJAH (U.A.E.)	1985	49.7	0.1	10.2
MUBAREK	SHARJAH, U.A.E.	1983	37	0.62	4.8
SOUEDIE	SYRIA	1983	24.9	3.82	5.3
HYDRA	TIMOR SEA (INDONESIA)	1994	37.5	0.08	3
GALEOTA MIX (TRINIDAD BLEND)	TRINIDAD TOBAGO	1983	32.8	0.27	2
ASHTART	TUNISIA	1982	30	0.99	ND
ALASKAN NORTH SLOPE	USA (ALASKA)	1992	27.5	1.11	4.4
COOK INLET	USA (ALASKA)	1985	35	0.095	7.7
HUNTINGTON BEACH	USA (CALIFORNIA)	1978	20.7	1.38	ND
SAN JOAQUIN VALLEY	USA (CALIFORNIA)	1978	15.7	1.2	1.2
WILLMINGTON	USA (CALIFORNIA)	1973	18.6	1.59	2.2
ELK HILLS STEVENS	USA (CALIFORNIA)	1977	37.1	0.4	7.9
HONDO BLEND	USA (CALIFORNIA)	1992	20.8	4.29	ND
HONDO MONTEREY	USA (CALIFORNIA)	1992	19.4011	4.7	ND
HONDO SANDSTONE	USA (CALIFORNIA)	1992	35.2	0.21	ND
SUNNILAND	USA (FLORIDA)	1987	24.9	3.25	7.45
LOUISIANA LIGHT SWEET	USA (LOUISIANA)	1981	36.1	0.45	3.8
OSTRICA	USA (LOUISIANA)	1975	32	0.3	3.9
SOUTH LOUISIANA	USA (LOUISIANA)	1982	32.8	0.28	3.3
LAKE ARTHUR (HUNT PRODUCTION)	USA (LOUISIANA)	1992	41.9	0.06	3.6
LAKEHEAD SWEET	USA (MICHIGAN)	1985	47	0.31	ND
NEW MEXICO MIXED INTE	USA (NEW MEXICO)	1979	37.6	0.167	4.1
BASIN-CUSHING COMPOSI	USA (OKLAHOMA)	1989	34	1.95	5.5
COASTAL B-2	USA (TEXAS)	1983	32.2	0.22	3.9
EAST TEXAS	USA (TEXAS)	1982	37	0.21	6.9
SEA BREEZE	USA (TEXAS)	1983	37.9	0.1	4.3
WEST TEXAS SEMI-SWEET	USA (TEXAS)	1982	39	0.27	ND
WEST TEXAS SOUR	USA (TEXAS)	1981	34.1	1.64	5.3
WEST TEXAS INTERMEDIA	USA (TEXAS)	1994	40.8	0.34	6.4
TOM BROWN	USA (WYOMING)	1988	38.2	0.1	4.6
WYOMING SWEET (AMOCO B)	USA (WYOMING)	1989	37.2	0.33	ND
BCF-24	VENEZUELA	1990	23.5	1.68	3.1
LAGO MEDIO	VENEZUELA	1989	32.2	1.01	5.2
LEONA	VENEZUELA	1990	24.4	1.51	2.5
MESA	VENEZUELA	1990	29.8	1.01	3.2
BACHAQUERO	VENEZUELA	1969	16.8	2.4	1.6
BACHAQUERO HEAVY	VENEZUELA	1975	12.8	2.66	0.2

BOSCAN	VENEZUELA	1983	10.1	5.5	0.4
CEUTA EXPORT	VENEZUELA	1979	27.8	1.37	ND
GUANIPA	VENEZUELA	1964	30.3	0.85	5.6
LAGO TRECO	VENEZUELA	1963	26.7	1.5	3.6
LAGUNILLAS HEAVY	VENEZUELA	1970	17	2.19	1
LA ROSA MEDIUM	VENEZUELA	1983	25.3	1.73	4
MEREY	VENEZUELA	1973	18	2.28	1.7
OFICINA	VENEZUELA	1967	33.3	0.78	5.8
PILON	VENEZUELA	1971	14.1	1.91	ND
TEMBLADOR	VENEZUELA	1967	21	0.83	1.2
ANACO WAX	VENEZUELA	1978	40.5	0.24	ND
TIA JUANA HEAVY (18)	VENEZUELA	1969	18.2	2.24	1.3
TIA JUANA LIGHT	VENEZUELA	1989	31.8	1.16	6.4
TIA JUANA MEDIUM 24	VENEZUELA	1971	24.8	1.61	3.4
TIA JUANA MEDIUM 26	VENEZUELA	1971	26.9	1.54	2.2
TIA JUANA PESADO (12)	VENEZUELA	1983	12.1	2.7	ND
TIA JUANA 102	VENEZUELA	1971	25.8	1.63	3.6
BACH HO (WHITE TIGER)	VIET NAM	1990	38.6	0.03	2.5
DAI HUNG (BIG BEAR)	VIET NAM	1990	36.9	0.08	ND
MASILA	YEMEN	1993	30.5	0.67	1.74
ZAIRE	ZAIRE	1983	31.7	0.13	2.2