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Chempak: Physical-Properties Database Structure and Development[1]

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Chempak (commercial physical properties database and properties estimation software) gives the thermodynamic and transport properties of pure compounds as functions of temperature and pressure for both liquid and vapor phases. Compound liquid properties are defined from the melting to the critical points. Vapor properties are defined from the melting point to 1300 K. The user may define up to 50 mixtures of compounds drawn from the database. In addition, the user may add up to 100 additional compounds defined by using the same techniques employed to construct the main database. Vapor properties are defined by the use of the Lee–Kesler and the Wu and Stiel equations of state. Vapor viscosity and thermal conductivity are defined using corresponding states methods. Liquid thermodynamic properties (except specific heat) are derived from the equation of state. All other liquid properties are defined by setting 11 data values from the melting to the critical point. The resulting property data arrays are interpolated against temperature.

KEY WORDS: databases; equation of state; thermodynamic properties; transport properties.

1. INTRODUCTION

Chempak physical properties database and properties estimation software comprises a core database, user-defined mixtures, and user-defined compounds, all with a full range of vapor and liquid properties, and an aqueous solution and heat transfer liquid database with liquid properties only.

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2. DATABASE SUMMARY

2.1. Core Database

The core database consists of 580 organic and inorganic compounds. Variable properties are available as functions of temperature and pressure. Liquid properties are defined from melting to critical temperatures. Vapor properties are defined to 1300 K and 20 × critical pressure. Crucial to the development of the database was the selection of an efficient and flexible method of storing and calculating liquid property values derived from a wide range of sources and methods. It was of importance that the database structure be independent of the precise form of the primary published data and estimated values. For vapor properties, the selection of suitable equations of state to cover both nonpolar and polar compounds in a flexible manner was of primary importance.

The following categories of compounds are available: alkanes, alkenes and alkynes, halogenated organics, ethers, ketones and aldehydes, alcohols and phenols, esters, benzene derivatives, heterocyclic and polycyclic compounds, organic nitrogen compounds, organic sulfur compounds, and inorganic compounds.

For every compound in the core database, the following constant properties are available: critical temperature, critical pressure, critical volume, normal boiling and melting points, molecular weight, acentric factor, dipole moment, enthalpy of formation, and Gibbs free energy of formation. The following variable properties are available: vapor pressure, specific volume, expansion coefficient, compressibility factor, specific heats, enthalpy, heat of vaporization, internal energy, entropy, viscosity, thermal conductivity, and surface tension. The properties may be calculated as functions of temperature and pressure for saturated and unsaturated conditions. Values of selected properties may be calculated over a temperature range at constant pressure or over a pressure range at constant temperature.

The database incorporates values based on published experimental measurements, experimentally derived property values, published correlations derived from experimental measurements, and property values derived from estimation methods. The experimental data and experimentally derived correlations used have been derived from published research articles, compilations, and handbooks. Wherever possible, data compilations giving evaluation of the presented data have been used. Calculated values for liquid properties are interpolated, smoothed values. Calculated values for vapor properties are derived from the equation of state or other corresponding-states methods. For each compound in the core database, the user can access information about the sources of the data and any estimation techniques used and the expected accuracy of the data values for each property. The on-line help features of the software and the software operating and reference manual provide a critical commentary on the estimation methods used including estimates of expected accuracy for each estimation method for different types of compounds.

2.2. Aqueous Solutions and Heat-Transfer Liquids

A subsidiary database of 70 aqueous solutions and heat transfer liquids with a reduced subset of properties is provided. The following properties are available: specific volume, expansion coefficient, specific heat, enthalpy, entropy, viscosity, thermal conductivity, and Prandtl number.

2.3. User-Defined Mixtures

This database allows the definition of up to 50 mixtures, each with up to 10 components drawn from the core database. The range of constant and variable properties available for user-defined mixtures is essentially the same as for the core database.

2.4. Properties Estimation and User-Defined Compounds

The user may define up to 100 new compounds and add these to the database. A range of correlations and estimation methods is available for each property. The level of definition of the constant and variable properties is the same as for the core database.

3. CONSTANT PROPERTIES

3.1. Critical Properties

The great majority of the values of critical temperature, pressure, and volume are published directly measured experimental values. When experimental values were not available, Joback group contribution estimates [1] were used for the critical temperature, pressure, and volume; the method of Tyn and Calus [2] was also used for critical volume (average errors, about 2%). Reid et al. [3] report that expected errors for the Joback method are approximately 5 K for the critical temperature, 5% for the critical pressure, and 2% for the critical volume.

3.2. Normal Boiling and Melting Points

All values of the normal boiling point are believed to be experimental directly measured values. Where possible, quoted melting points are experimental directly measured values. No accurate method for estimation of compound melting points is available. In the absence of experimental data, a rough estimate was derived from the Joback method [1] (typical errors are 23 K).

3.3. Dipole Moment

All quoted values are believed to be experimentally derived.

3.4. Acentric Factor

In all cases, the acentric factor is calculated from the vapor pressure correlation.

3.5. Heats of Formation

The great majority of values of the enthalpy of formation and the Gibbs free energy of formation are experimental directly measured values; otherwise, Joback group contribution estimates [1] are used.

4. LIQUID PROPERTIES

Wherever possible, individual directly-measured experimental data or correlations derived from experimental data were used. Liquid properties are available in many correlation forms often over limited ranges of temperature. The range from room temperature to the normal boiling point is usually well covered in the published literature. Property values near the critical and melting points are often not available. In order to represent the values over the entire range of temperature from the melting point to the critical point, it was necessary to combine property value estimates with experimentally derived correlations.

In the Chempak database, liquid properties are represented as a series of 11 property values equally spaced over the temperature range from the melting point to the critical point. Values at specific temperatures are computed using spline, Lagrangian, or other interpolation techniques. Vapor pressure and liquid viscosity are interpolated as logarithms, and liquid specific heat, which exhibits a singularity at the critical point, was transformed to a finite function prior to interpolation. The 11-point structure used in Chempak allows the maximum freedom in selection and combination of data points derived from different sources and estimation methods. Experimentally derived correlations and experimental data points can be combined with general estimation methods using interpolation to produce a single credible function over the entire temperature range. The interpolation techniques are specific to the requirements of each property. Pressure corrections are applied as necessary.

4.1. Vapor Pressure

Published correlations derived from experimental data were available for most compounds, at least over a proportion of the temperature range; otherwise, the equations of Gomez–Thodos [6–8] were used. Tests by the author showed the clear superiority of the Gomez–Thodos equations to the Lee–Kesler [4] equation even for nonpolar compounds. In the database, vapor pressure is stored and interpolated in reduced logarithmic form.

4.2. Liquid Specific Volume, Expansion Coefficient, and Compressibility Factor

Published experimentally derived correlations were available for the great majority of the compounds. In the absence of published data, the Rackett equation [3] can be used over the entire temperature range (typical errors are less than 3%). Where a single good-quality volume data point is available, an improved Rackett correlation can be calculated. Pressure corrections are applied when appropriate. Expansion coefficients and compressibility factors were derived from the liquid specific volume.

4.3. Liquid Specific Heats

Published correlations derived from experimental data were available for most compounds, at least over part of the temperature range. In the absence of published data, values can be calculated from the Missenard group contribution method [9] (applicable up to the normal boiling point) or the Rowlinson–Bondi corresponding-states method [3] (applicable in most cases over the entire temperature range). Note that liquid specific heat approaches infinity as the temperature approaches the critical point. To establish the required 11-point interpolation table, the actual values used in the interpolation table are a function of specific heat and reduced temperature. This transformation guarantees a smooth finite function over the entire range of temperature. The primary specific heat values are those at constant pressure. The liquid specific heat at constant volume is calculated from the value at constant pressure using a correction derived from the equation of state. The calculated specific heats are corrected for pressure using a correction derived from the equation of state.

4.4. Liquid Thermodynamic Properties

Liquid enthalpy, internal energy, heat of vaporization, and entropy are all derived from the equation of state using the low-pressure values of the corresponding vapor properties.

4.5. Liquid Viscosity

No general method exists to estimate liquid viscosity over the entire temperature range. Generally, group contribution methods work best below the normal boiling point; corresponding-states methods are best above this temperature. Some experimental liquid viscosity data are available for most compounds. The database values are stored and interpolated in logarithmic form. Pressure corrections are applied as appropriate. In the absence of published data, the following methods are applicable.

- Van Velzen Group Contribution Method [10]: This is a complex and fairly comprehensive group contribution method. Typical errors are in the range of 5 to 15%. The method is applicable up to the normal boiling point.
- Przezdziecki Method [11]: This method correlates liquid viscosity as a function of liquid specific volume. Errors may range up to 25%. The method is applicable in the middle range of temperatures.
- Letsou and Stiel Corresponding-States Method [12]: Errors typically lie in the range of 5 to 10%. The method is applicable above the normal boiling point.

4.6. Liquid Thermal Conductivity

Most compounds have published experimental values of thermal conductivity or correlations derived from experimental data over at least part of the temperature range. Liquid thermal conductivity values in the region of the critical temperature are not available for many compounds. When no published data are available, the following estimation methods are applicable. Pressure corrections are applied as appropriate.

- Sato–Riedel Method [3]: Errors lie in the range of 5 to 15%. Estimates are poor for low molecular weight and branched hydrocarbons. Results are better for nonhydrocarbons. The method is applicable up to the normal boiling point.
- Baroncini Correlations [13]: The method is applicable up to the normal boiling point for specific categories of compounds; nitrogen and sulfur compounds and aldehydes cannot be handled. Errors are usually less than 10%.
- Ely and Hanley Estimation [14]: The method is applicable above the normal boiling point. Errors for hydrocarbons are typically less than 10%. Accuracy for nonhydrocarbons is not well established Accuracy for polar compounds may be poor.

4.7. Liquid Surface Tension

Most compounds have published experimental values of surface tension or correlations derived from experimental data available over the entire temperature range. In addition, by definition, the surface tension at the critical point is zero. In the absence of published data, reasonable values can be provided by the Brock and Bird corresponding-states method [15] for nonpolar compounds and the Hakim corresponding-states method [16] for polar compounds.

5. VAPOR PROPERTIES

Our selection of equations of state after review of many such equations came down to the Lee–Kesler equation of state [4] for nonpolar compounds and the Wu and Stiel [5] equation of state for polar compounds. The Lee–Kesler equation is based on linear interpolation of properties between two nonpolar reference fluids using the acentric factor as the interpolating variable. The Lee–Kesler equation covers a wide range of temperature and pressure and gives good predictions for both saturated and unsaturated states. The Wu and Stiel equation is an extension of the Lee–Kesler equation: a third polar reference fluid (water) is added with the Stiel polarity factor as the interpolating variable to represent polar effects. The Keenan equation of state for water [17] is incorporated to provide the required water properties. Wu and Stiel present good confirming data for their method; further checks by the author agree.

5.1. Vapor Specific Volume, Expansion Coefficient, and Compressibility Factor

The specific heat for the vapor phase is determined from the equation of state. Errors are usually less than 2%. Errors in the critical region will be higher. The vapor expansion coefficient and compressibility factor are derived from the vapor specific volume.

5.2. Low-Pressure Vapor Properties

The low-pressure vapor specific heat is defined by establishing values at 11 temperature points equally spaced from 50 to 1300 K. The great majority of compounds have published experimentally derived correlations available typically from 273 through 800 to 1000 K. Values above 1000 K or below 273 K are not so readily available. In the absence of published values, the following methods will provide good estimates.

- The Joback group contribution method [1] gives good values over the range of 273 to 1000 K. Errors are typically in the range of 1 to 2%.
- Simple power-law extrapolation gives reasonable values to 1300 K.
- Special power-law extrapolation methods developed by the author from analysis of low temperature specific heat values for 80 compounds yield accurate values (better than 2%) down to 100 K and reasonable values (about 5% errors) at 50 K.

Low-pressure vapor enthalpy, internal energy, and entropy are derived from low-pressure vapor specific heat by integration.

5.3. Vapor Thermodynamic Properties

The vapor specific heats, enthalpy, internal energy, and entropy are derived from the equation of state and the low-pressure vapor thermodynamic properties.

5.4. Vapor Viscosity and Thermal Conductivity

The vapor viscosity and thermal conductivity are established in Chempak from corresponding-states estimation methods.

6. USER-DEFINED MIXTURES

Chempak allows the definition of mixtures of up to 10 components drawn from the core database. Compositions may be specified as weight or mole percentage. Constant properties for the mixture (including pseudocritical properties) are calculated using the Lee–Kesler mixing rules [4]. Recommended mixing rules are used to formulate the variable properties of the mixture. The range of properties available for user-defined mixtures is the same as for the core database.

7. PROPERTIES ESTIMATION AND USER-DEFINED COMPOUNDS

The user-defined compounds software allows the user to go through the same compound properties definition process as was used in formulating the core database. Up to 100 user-defined compounds can be entered and stored in the database. A set of data points can be fitted by least squares and the fitting function entered into the database. Interpolation and extrapolation methods are available for each property. Individual data points may be entered at any grid point by the user.

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