Properties Database Structure and Development [1]

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A

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ABSTRACT

Chempak (commercial physical properties database) 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 Wu & Stiel equations of state.Vapor viscosity and 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, Physical Properties, 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 solutions & heat transfer liquids database with liquid properties only.

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 temperature. Vapor properties are defined to 1300 K and 20 times 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 non-polar and polar compounds in a flexible manner was of primary importance.

The following categories of compounds are available: alkanes, alkenes/alkynes, halogenated organics, ethers, ketones/aldehydes, alcohols/phenols, esters, benzene derivatives, heterocyclic/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, Pressure & Volume, Normal Boiling & Melting Points, Molecular Weight, Acentric Factor, Dipole Moment, Enthalpy & 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, Conductivity, 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.

2.2 Aqueous Liquids and Heat-Transfer Liquids

A subsidiary database of 70 aqueous liquids 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, Conductivity, Prandtl Number. Values of selected properties may be calculated over a temperature range.

2.3 User-Defined Mixtures

This facility allows the definition of up to 50 mixtures each of up to 10 component compounds 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 & User-Defined Compounds

The user may define up to 100 new compounds and to add these to the database. A range of correlations and estimation methods are 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 experimental values. Where experimental values were not available, Joback group contribution estimates [1] were used for 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 expected errors for the Joback method are 5 K for Critical Temperature, 5% for Critical Pressure and 2% for Critical Volume.

3.2 Normal Boiling & Melting Points

All values of boiling point are believed to be experimental. Where possible, quoted melting points are experimental. No accurate method of estimation of compound melting point 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 experimental

3.4 Acentric Factor

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

3.5 Heats of Formation

The great majority of values of Enthalpy of Formation and Gibbs Energy of Formation are experimental; otherwise, Joback group contribution estimates [1] are used.

4 LIQUID PROPERTIES

Wherever possible, experimental data or correlations 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 eleven-point structure used in Chempak allows the maximum freedom in selection and combination of estimation methods. Experimental correlations and datapoints 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 experimental data was available for most compounds at least over a proportion of the temperature range; otherwise, the equations of Gomez-Thodos [6,7,8] were used. Tests by the author showed the clear superiority of the Gomez-Thodos equations to the Lee-Kesler [4] equation even for non-polar compounds. In the database, vapor pressure is stored and interpolated in reduced logarithmic form.

4.2 Liquid Specific Volume, Expansion Coefficient & 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 datapoint is available, an improved Rackett correlation can be calculated. Pressure corrections are applied when appropriate. Expansion coefficient and compressibility factor were derived from the liquid specific volume.

4.3 Liquid Specific Heats

Published correlations 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. 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 with 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 liquid viscosity data is 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 5 to 15%. The method is applicable up to normal boiling point
- Przezdziecki Method [11]. This method correlates liquid viscosity with changes in liquid specific volume. Errors may range up to 25%. The method is applicable in the middle range of temperatures
- Letsou & Stiel Corresponding States Method [12]. Errors typically lie in the range 5 to 10%. The method is applicable above normal boiling point.

4.6 Liquid Conductivity

Most compounds have published experimental conductivities over at least part of the temperature range. Liquid 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 5 to 15%. Estimates are poor for low-molecular weight and branched hydrocarbons. Results are better for non-hydrocarbons. 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 & Hanley Estimation [14]. The method is applicable above the normal boiling point. Errors for hydrocarbons are typically less than 10%. Accuracy for non-hydrocarbons is not well established. Accuracy for polar compounds may be poor.

4.7 Liquid Surface Tension

Most compounds have published surface tension values 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 & Bird corresponding states method [15] for non-polar 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 non-polar compounds and the Wu & Stiel [5] equation of state for polar compounds. The Lee-Kesler equation is based on linear interpolation of properties between two non-polar 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 & 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

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. 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 K to 1300 K. The great majority of compounds have published experimentally-derived correlations available typically from 273 K 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:

- Joback group contribution method [1] gives good values over the range 273 to 1000 K. Errors are typically in the range 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 & Conductivity

Vapor viscosity and conductivity are established in Chempak from corresponding states estimation methods.

6 USER-DEFINED MIXTURES

Chempak allows the definition of mixtures of up to 10 component compounds drawn from the core database. Compositions may be specified as weight or mole percent. 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 & USER-DEFINED COMPOUNDS

The user-defined compounds facility 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 datapoints can be fitted by least squares and the fitting function entered to the database. Interpolation and extrapolation methods are available for each property. Individual datapoints may entered at any gridpoint by the user.

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