Databanks, Physical Property models and Transport property estimation

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Agenda

- Data banks
  - Aspen +
  - Other sources of data
- Models for physical properties evaluation
  - Pure components
  - Mixtures
- Physical Properties: Transport properties
  - Viscosity and thermal conductivity
  - Diffusion coefficients
  - Surface tension

Databanks in Aspen +

- **AQUEOUS** Databank:
  - Contains parameters for 1,688 ionic species.
  - It is used for electrolytes applications.
  - The key parameters are the aqueous heat and Gibbs free energy of formation at infinite dilution and aqueous phase heat capacity at infinite dilution
- **Binary coefficient** databanks:
  - AP-EOS Databank: Pure-component and binary parameters for the Cubic-Plus-Association property model
  - EOS-LIT Databank: Binary parameters for various models using EOS
  - PC-SAFT Databank: Pure and binary parameters for PC-SAFT-based models for all types of fluids
  - POLYPCSF Databank: Pure and binary parameters for PC-SAFT-based models for normal fluids
- **BIODIESEL** Databank:
  - Contains parameters for 461 organic compounds typically found in biodiesel production processes, including numerous triglycerides, diglycerides, and monoglycerides

Databanks in Aspen +

- **COMBUST** Databank:
  - special databank for high temperature, gas phase calculations.
  - It contains parameters for 59 components typically found in combustion products, including free radicals.
  - The CPIG parameters were determined from data in JANAF tables for temperatures up to 6000K (JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan, 1979).
  - Calculations using parameters in the ASPENPCD and PURECOMP are generally not accurate above 1500K.
- **ELECPURE** Databank:
  - contains 28 parameters used in many common models for 17 components commonly found in amine processes
- **ETHYLENE** Databank:
  - Contains 85 pure component and binary interaction parameters required to model the typical ethylene process.
  - The parameters are for the SRK property method which include the critical temperature, critical pressure, acentric factor and binary interaction parameters.
  - The ETHYLENE databank should be used with the PURE databank and the SRK property method
- **HYSIS** Databank:
  - Contains 30 pure component and 4 binary parameters used in Aspen HYSYS property methods for 1671 components.

Databanks in Aspen +

- **INITIATOR** Databank:
  - Property parameters and thermal decomposition reaction rate parameters for polymer initiator species. Collected from various sources.
- **INORGANIC** Databank:
  - Contains thermochemical data for 2,477 (mostly inorganic) components.
  - The key data are the enthalpy, entropy, Gibbs free energy, and heat capacity correlation coefficients.
  - For a given component, there can be data for a number of solid phases, a liquid phase, and the ideal gas phase.
- **NRTL-SAC** Databank:
  - pure component parameter XYZE for more than 100 common solvents.
  - This parameter contains a representation of each of these solvents as a combination of the four types of segments used in the NRTL-SAC property method
- **POLYMER** Databank:
  - Pure component parameters for polymer species. Collected from various sources, including Polymer Handbook.

Data Banks in Aspen +

- **PURE10** databank
  - Contains parameters for over 1727 (mostly organic) components. Based on AIChE DIPPR data compilation project. The parameters stored in the databank can be categorized as:.
    - Universal constants, such as critical temperature, and critical pressure
    - Temperature and property of transition, boiling point and triple point
    - Reference state properties, enthalpy and Gibbs free energy of formation
    - Coefficients for temperature-dependent thermodynamic properties, such as liquid vapor pressure
    - Coefficients for temperature-dependent transport properties, such as liquid viscosity
    - Safety properties, such as flash point and flammability limits
    - Functional group information for all UNIFAC models
    - Parameters for RKS and PR equations of state
    - Petroleum-related properties, such as API gravity and octane numbers
    - Other model-specific parameters, such as the Rackett and UNIQUAC parameters
  - The content of the main pure component databank is continually updated, expanded, and improved.

Data Banks in Aspen +

- **SEGMENT** Databank: Property parameters for polymer segments.
- **SOLIDS** databank
  - Contains parameters for 3314 solid components. This databank is used for solids and electrolytes applications. This databank is largely superseded by the INORGANIC databank, but is still essential for electrolytes applications.
- **UNIFAC** databank
  - Contains binary interaction group parameters for UNIFAC (different versions)
- **NIST-TRC**:
  - contains pure component data for 25,821 compounds (mostly organic), including the approximately 2000 compounds already available in the main pure component databank

Data sources (books & on-line databanks)

- **CRC Handbook of Chemistry and Physics**
  - database of chemical compounds and structures with basic chemical and physical data points.
- **DIPPR Physical and Thermodynamic Properties**
  - experimental data and correlations of temperature-dependent properties for over 1,800 pure chemicals, mostly organic, with a couple hundred inorganic as well.
- **Knovel Critical Tables**
  - tables of physical, solvent, and thermodynamic properties. The physical property tables include over 21,000 inorganic and organic compounds
- **NIST Chemistry WebBook**
  - Reliable thermophysical and spectral data for a few thousand important compounds.
- **NIST TRC Web Thermo Tables**
  - critically evaluated thermodynamic property data for over 23,000 pure organic compounds. Available in A+ too.
- **IUPAC-NIST Solubility Data Series**
  - Searchable version of data from 18 selected volumes from the longstanding SDS book series.

Web open data sources and apps

- **Carbon Dioxide Properties Calculator**
  - Free calculator for thermodynamic and transport properties of carbon dioxide.
- **Chemo**
  - Searchable thermodynamic properties of about 90,000 molecules from NIST data.
- **DETHERM**
  - Database of checked thermophysical data on over 21,000 pure substances and 100,000 mixtures, corresponding in part to the printed Chemistry Data Series. Downloading the data is on a pay-per-view basis. Some of the older data may be found in the DECHEMA CDS volumes.
- **Dortmund Data Bank**
  - DDB is a proprietary collection of evaluated phase equilibria and transport property data for multicomponent systems. Many of these data sets are also available via the similar DETHERM system.
- **Engineering ToolBox**
  - Wide array of property tables and calculators for common materials.
- **IAPWS Water Properties**
  - Recommended formulations for numerous properties of water, steam, and aqueous solutions. (Int. Assoc. for the Properties of Water and Steam)

NIST data base

- **NIST Clathrate Hydrate Physical Property Database**
- **NIST CODATA Fundamental Physical Constants**
  - A self-consistent set of values of the basic constants and conversion factors of physics and chemistry recommended by the Committee on Data for Science and Technology (CODATA).
- **NIST Critically Selected Stability Constants of Metal Complexes Database.**
  - Covers interactions for aqueous systems of organic and inorganic ligands with protons and various metal ions. Includes 22,898 protonation constants under specified conditions of temperature and ionic strength for over 4,700 ligands, along with 3429 heats of protonation and 3016 entropies of protonation. The legacy NIST 46 Version 8.0 software (2004) is available free on the NIST site as an .exe file, as well as a user guide..
- **NIST - ILThermo**
  - web-based ionic liquids database available free to the public.
- **NIST Chemical Kinetics Database**
  - includes essentially all reported kinetics results for thermal gas-phase chemical reactions. The database contains in excess of 38,000 separate reaction records for over 11,700 distinct reactant pairs.

NIST data base

- **NIST-JANAF Thermochemical Tables**
  - The JANAF (Joint Army-Navy-Air Force) Tables tabulate temperature-dependent thermochemical properties for over 47 elements and their associated compounds. The 1800+ tables cover the crystal, liquid, or ideal gas states for single and multi-phases of many inorganic substances and organic substances with one or two carbon atoms.
- **NIST Physical Reference Data**
  - Web site compiles and organizes many kinds of critically evaluated and up-to-date physical data, with searchable bibliographic sources. Physical constants, atomic and molecular spectroscopic data, ionization data, x-ray and gamma-ray data, nuclear physics data, and condensed matter data, etc.
- **NIST Solution Kinetics Database**
  - Contains data on rate constants for solution-phase chemical reactions. The database contains more than 11,500 unique chemical species.
- **NIST Thermophysical Properties of Fluid Systems**
  - Part of the NIST WebBook, this database offers accurate isobaric, isothermal and saturation properties of a number of common fluids, gases, refrigerants, and important hydrocarbons.
- **NIST ThermoML**
  - experimental thermophysical and thermochemical property data reported in the corresponding articles published by several major journals in the field.

Data bases miscellaneous

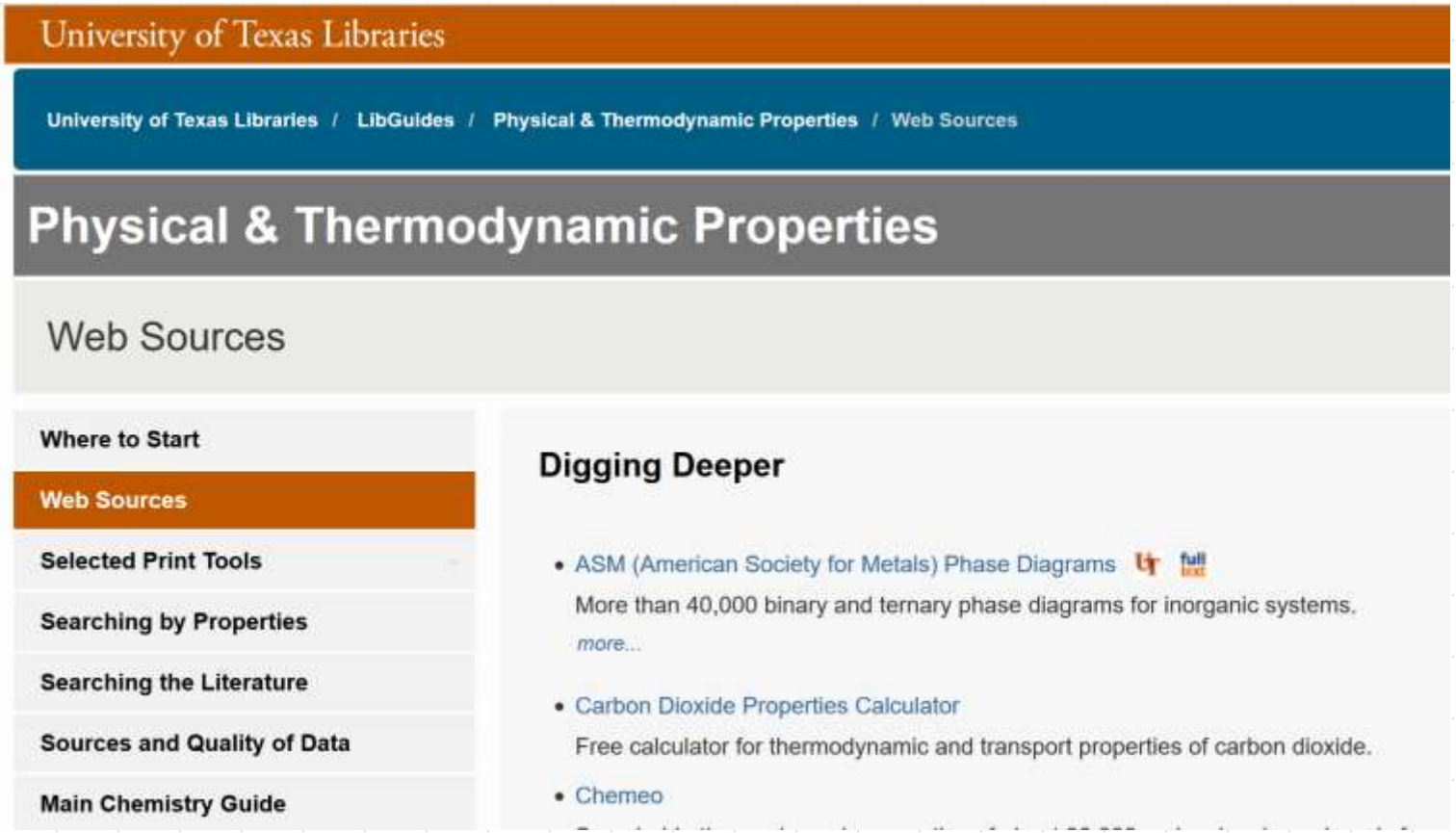
- **Journal of Physical and Chemical Reference Data.**
  - This journal, co-published by NIST and the American Institute of Physics, contains articles and monographs reporting extensive critical property data.
- **Kaye & Laby** (archived)
  - 16th edition (1995) of the popular handbook of tables. (Archived site)
- **KDG** (Korean Thermophysical Properties Databank)
  - Provides thermophysical property data and calculation methods for hydrocarbons, light gases, polymers and electrolyte solutions commonly encountered in chemical engineering practices. Includes sections on pure component properties, VLE, and equilibrium data. Data are unattributed and of unknown provenance.
- **MatWeb**
  - MatWeb's database includes manufacturer-supplied property data on about 24,000 materials, including thermoplastic and thermoset polymers, metals, steel, superalloys, titanium and zinc alloys, ceramics, semiconductors, fibers, and other engineering materials. Searchable by material type, trade name, property parameters, manufacturer, etc.

Data bases miscellaneous

- **Phase Equilibria Diagrams Online**
  - A collection of more than 23,000 critically-evaluated phase diagrams in support of ceramics research.
- **pKa Table** (Bordwell)
  - tables of acidity in DMSO for organic structures, arranged by classification. Derived from studies by F.G. Bordwell.
- **Polymers**: A Property Database
  - e-book of properties and applications of important polymers. (CRC ChemnetBase)
- **Steam Tables Online**
  - Free online calculator using IAPWS-IF97 and IAPWS-95 formulations.
- **Thermal Resources**
  - A suite of free resources that includes a Materials Database with over 1000 searchable materials, with corresponding thermal conductivity, thermal diffusivity, thermal effusivity, specific heat and density information; a literature database of papers on thermal conductivity; simulation software; and a properties calculator. (Thermtest).
- **Thermo Chemical Properties Estimations**
  - A collection of Java applets that generate estimates of various properties.

An useful directory of links

- Links to resources: https://guides.lib.utexas.edu/chemistry/properties/web



Data Banks in ASPEN+: DEMO

User Environment

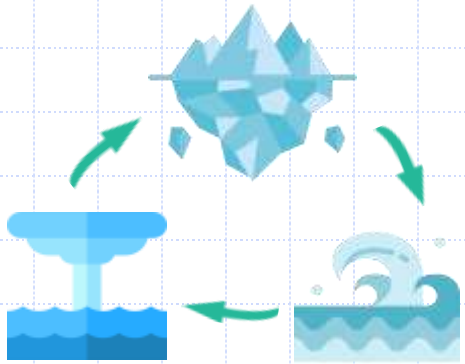
Data Banks

Retrieval of components from Data banks

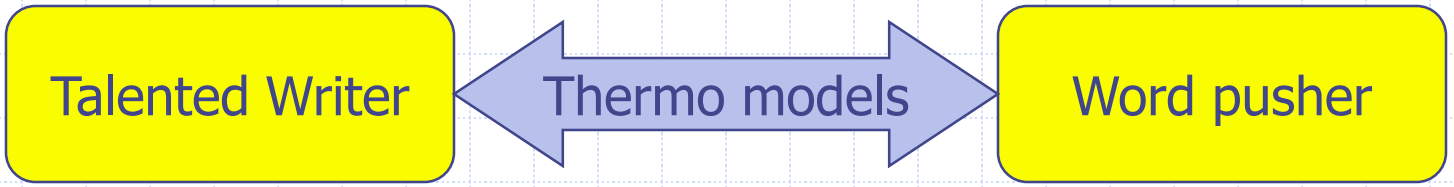
Models for physical properties evaluation

Pure components

Mixtures



Motivations…



- Excess volume for aqueous mixtures
  - **Near azeotropic distillation of ethanol** – water mixtures with data expressed in terms of volumetric fraction
  - The simulator predict a **mass fraction much closer to the azeotrope** → more energy consumption
- Heavy in the top
  - Separation of 1-2 butadiene from 1-3 butadiene (1-2 is heavier)
  - The simulator uses estimated critical properties **and 1-2 goes to the top**!!!

A property model is made up of:

- One or more mathematical equations where the property of interest is a function of the **state variables** (T, P, x), and of a number of **parameters**.
  - Parameters are defined as physical variables whose value is however related to (and fixed for) the specific component or mixture.
  - also constants (either universal such as R or property-specific) can be present;
- Model **parameter values** for the specific component or mixture.
  - If even one of them is not known, the model is useless for application;
- A **applicability range** of the model,
  - defined with respect to involved state variables, in which the model ensures an accurate evaluation of the property.
  - A model should never be used outside these ranges;
- Information about the **accuracy** in the calculation of the property of interest, in terms of ± % error.
  - This is important as it allows to evaluate how much the process calculation is affected by the property model inaccuracy, i.e. the sensitivity of process simulation to these errors.

Models for the evaluation of pure component properties

- Definition of correlation, prediction and full prediction
  - We agree to call "**prediction**" the calculation of a property by a model which does not require any experimental data of the same property.
  - We call "**correlation**" the calculation of a property by a model which requires experimental data of the same property.
  - Predictive and correlative models are defined accordingly.
  - "**Full prediction**" means that the information about the component structure (i.e. the functional groups in its chemical formula) is sufficient to calculate the property of interest.
- However, about the definition of prediction there is a difference between the cases of pure components and mixtures.

Models for the evaluation of pure component properties

- Example: vapor density by means of the **Virial EOS**
  - This is a predictive model:

$$\rho = \frac{MW}{v} = \frac{MW \cdot P}{RTZ}$$

$$Z = 1 + \frac{BP}{RT}$$

$$B = B^{(0)}(T/T_C) + \omega B^{(1)}(T/T_C)$$

- Example: saturated liquid density by means of the **Rackett** equation
  - This is a correlative model:

$$v^{L,sat} = \frac{RT_c}{P_c} Z_{RA}^{[1+(1-T/T_c)^{2/7}]}$$

- Other examples of correlative models:
  - equations of state with higher number of parameters, such as the BWR EOS

Models for the evaluation of mixture properties

- Two ways to calculate a mixture property:
  - from the same property of all the pure components, at the same P, T and aggregation phase, by **weighting them** on some mixture composition:

$$M_m = \sum_i x_i M_i^* + M^E$$

  - using a property model which is accurate to evaluate the same property of pure components, by **weighting the values of the model parameters** on some mixture composition

$$Par_m = \sum_i \sum_j x_i x_j Par_{i,j} \qquad Par_{i,j} = \frac{Par_i + Par_j}{2} \qquad Par_{i,j} = \sqrt{Par_i Par_j}$$

  - Then the value of the mixture property is directly obtained by applying the pure component model, but with the values of mixture parameters in it.
- Two big issues affect the first approach:
  - the value of some the pure component property at the mixture conditions is unavailable, because components at the mixture conditions are in a different aggregation state
  - the excess value M^E of that property is not known

Models for the evaluation of mixture properties

- Definition of correlation, prediction and full prediction
  - "**Prediction**" means that the property can be calculated from the pure component corresponding one and the mixture composition only.
  - "**Correlation**" means that data of the same mixture property are needed to perform the property calculation.
  - Almost all the predictive models proposed so far for mixtures are not accurate enough for process simulation purposes. So, it is useful to define another type of "prediction", less demanding, which is the ability of a model to calculate a property of a multicomponent mixture by using experimental information of only (but all) the binary systems made by all component pairs present in the mixture.
  - With "**full prediction**" we mean that the information about the components structure (i.e. the functional groups in their chemical formula), together with the mixture composition, is sufficient to calculate the mixture property of interest.

Models for the evaluation of mixture properties

- Example: vapor density by means of the Virial EOS
  - This is a predictive model:

$$Z_m = 1 + \frac{B_m P}{RT} \qquad B_m = \sum_i \sum_j x_i x_j \sqrt{B_i^* B_j^*}$$

- Example: saturated liquid density by means of the Rackett equation
  - This is a predictive model:

$$v_m^{L,sat} = \frac{RT_{C,m}}{P_{C,m}} Z_{RA,m}^{[1+(1-T/T_{c,m})^{2/7}]}$$

$$Z_{RA,m} = \sum_i x_i Z_{RA,i}$$

$$T_{C,m} = \sum x_i x_j \sqrt{T_{C,i} T_{C,j}}$$

$$P_{C,m} = \sum x_i P_{C,i}$$

Models for the evaluation of mixture properties

- The extensions of both the Viral EOS and the Rackett equation models as outlined above are predictive but not accurate enough for process simulations.
- So, these models are modified by adding binary correction terms referred to as k_{ij}s (they are also called binary interaction parameters, but they are just adjustable parameters).
  - For the virial EOS this means:

$$B_m = \sum_i \sum_j x_i x_j \sqrt{B_i^* B_j^*} (1 - k_{ij})$$

  - and for the Rackett equation:

$$Z_{RA,m} = \sum_i x_i Z_{RA,i}$$

$$T_{C,m} = \sum x_i x_j \sqrt{T_{C,i} T_{C,j}} \left(1 - k_{ij}\right)$$

$$P_{C,m} = \sum x_i P_{C,i}$$

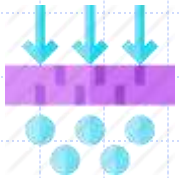
Physical Properties: Transport properties

Viscosity and thermal conductivity

Diffusion coefficients

Surface tension

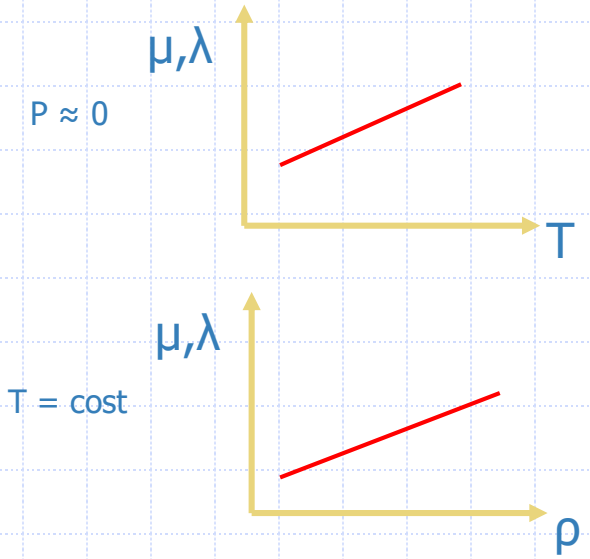
Generality on transport properties



- Calculated either from an **empirical equation** or from a **semi-empirical** (theoretical) correlation
- The coefficients for the empirical equation are determined **from experimental** data and are stored in the databank
- The mixture properties are calculated using appropriate **mixing rules**
- The properties that have the most in common in their behavior are **viscosity and thermal conductivity**

Viscosity and Thermal Conductivity

- Approaching **zero pressure**, viscosity and thermal conductivity are linear functions of temperature with a positive slope
- At a given temperature, viscosity and thermal conductivity **increase with increasing density**
- Detailed **molecular theories** exist for gas phase viscosity and thermal conductivity at low pressures
- Some of these account also for polarity
  - Chapman-Enskog-Brokaw (viscosity)
  - Chung-Lee-Starling (viscosity)
  - Stiel-Thodos (thermal conductivity)
- Calculate the difference of a certain property with respect to the low pressure value
- Require **mixing rules** for calculating mixture properties



Aspen accounts these properties for calculation of fluidodynamics of columns or pressure drops

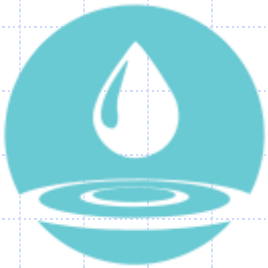
Viscosity and thermal conductivity

- Another class of models calculate the high pressure property directly from **molecular parameters and state variables**
  - TRAPP models
    - hydrocarbons
    - use critical parameters and acentric factor as molecular parameters
  - Chung-Lee-Starling models
    - use critical parameters, acentric factor, and dipole moment as molecular parameters.
- Liquid properties are often described by **empirical, correlative models**:
  - Andrade/DIPPR for liquid viscosity
  - Sato-Riedel for thermal conductivity.
  - Corresponding-states models can describe both liquid and vapor properties
    - Chung-Lee-Starling
    - TRAPP

Diffusion Coefficient

- **Diffusion is related to viscosity**
  - Diffusion coefficient models require viscosity, for both liquid and for vapor diffusion coefficients
  - Chapman-Enskog-Wilke-Lee
  - Wilke-Chang models
- **Vapor diffusion** coefficients can be calculated from molecular theories
  - Similar to those discussed for low pressure vapor viscosity and thermal conductivity
  - Similarly, pressure correction methods exist
  - The Dawson-Khoury-Kobayashi model calculates a pressure correction factor which requires the density as input.
- **Liquid diffusion** coefficients depend on activity and liquid viscosity
- **Binary diffusion** coefficients
  - required in processes where mass transfer is limited.
  - Binary diffusion coefficients describe the diffusion of one component at infinite dilution in another component.
- **Multicomponent** systems this corresponds to a matrix of values.
  - The average diffusion coefficient of a component in a mixture does not have any quantitative applications; it is an informative property.
  - It is computed using a mixing rule for vapor diffusion coefficients and using mixture input parameters for the Wilke-Chang model.

Surface Tension Methods



- Surface tension is calculated by **empirical**, correlative models
- Hakim – Steinberg – Stiel / DIPPR
  - An empirical linear mixing rule is used to compute mixture surface tension.

The DIPPR (Design Institute for Physical Properties) database provide all the parameters required for a proper fitting of empirical data for various properties: its adoption is warmly suggested instead of other less accepted databases