4
Databases in the Field of Thermophysical Properties in Chemical Engineering

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4.1
Introduction

Process synthesis, design, and optimization, and also detail engineering for chemical plants and equipment depend heavily on availability and reliability of thermophysical property data of pure components and mixtures involved. To illustrate this fact we can analyze the needs for one of the essential process engineering processes, the separation of fluid mixtures. For the design of such a typical separation process, e.g., distillation, we require thermodynamic properties of mixture, in particular for a system that has two or more phases at a certain temperature or pressure. We require the equilibrium constants of all components in all phases.

The quality of data inside the data calculation modules is essential and can have extensive effects. Inaccurate data may lead to very expensive misjudgements whether it is to proceed with a new process or modification of it or not to go ahead. Inadequate or unavailable data may cause a promising and profitable process to be delayed or in the worst case be rejected, only for the reason that it was not properly modelled in a simulation. Another potential danger, partially generated by the marketing statements of simulation software producers, is that the credibility of the results of a thermophysical model calculation generated by computer software is very high, even if the result is wrong. So the expert has the duty to prove that the most sophisticated software will not lead automatically to the most cost-effective solution in order to save effectively energy, if there is not a background with an accurate database of physical and thermodynamic data.

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4.2 Overview of the Thermophysical Properties Needed for CAPE Calculations

Without access to a numerical database and if the available literature and notes do not contain a value, the only possibility is to measure properties or to calculate them with a group contribution method or another estimation routine. The first alternative is expensive and time-consuming; the second one will produce data with unknown reliability in most cases, especially when molecules with two or more nonhydrocarbon functional groups in near proximity are involved. With the help of thermophysical databases with experimental values of pure component and mixtures, this problem can be solved. A description of what data are needed and which types of data are available follows. The properties required for the design of a thermal or chemical process depends upon the specific case and the temperature, pressure and concentration range. A short overview of the data needed in the simulation and design of processes is given in Table 4.1.

Table 4.1 Important categories of property data

Property type	Specific properties
Phase equilibria	Boiling and melting points, vapor pressure, fugacity and activity coefficients, solubility (Henry's constants, Ostwald or Bunsen coefficients)
PVT behavior	Density, volume, compressibility, critical constants
Caloric properties	Specific heat, enthalpy, entropy
Transport properties	Specific heat, latent heat, enthalpy, entropy, viscosity, thermal conductivity, ionic conductivity, diffusion coefficients
Boundary properties	Surface tension
Chemical equilibrium	Equilibrium constants, association/dissociation constants, enthalpies of formation, heat of reaction, Gibbs energy of formation, reaction rates
Acoustic	Velocity
Optical	Refractive index, polarization
Safety characteristics	Flash point, explosion limits, autoignition temperature, minimum ignition energy, toxicity, maximum working place concentration
Molecular properties	Virial coefficients, binary interaction parameters, ion radius and volume

4.3
Sources of Thermophysical Data

For years, the most popular way to find thermophysical property data was to take a look inside favorite book collections, starting with the Handbook of Chemistry and Physics up to data collection handbooks issued by data producers as DIPPR [1] and TRC [2], the Landolt-Börnstein [3] and the DECHEMA Chemistry Data Series [4]. Despite the inconvenience in using handbooks for data searches, a lot of users still appreciate the fast access to the data and, in comparison to the databases, relatively moderate price. An overview by Hochschule Merseburg University of Applied Science gives a list of available books and publications on thermophysical property data (www.fh-merseburg.de/PhysChem).

Nowadays, mainly under the pressure of having data available in a short time for calculations and due to the full-time access to networks, the easiest way to find data is with access to databases, accessible or as in-house versions or on-line via hosts or via the World-Wide Web.

Two types of collections and/or databases can be distinguished: bibliographical ones and numerical ones. A bibliographical collection or database is a literature source containing only references. Knowing the chemical species one needs data for, one can find literature references containing that data. Afterwards one has to go to the library and look up the different references to get the data. A numerical database or collection typically contains the literature references as well as measurement data. The numerical data could be accessed and used directly. In some cases this approach is combined with a critical review and selection of the available data, so that only thermodynamically consistent and proven data are contained in the collection. The approach could also be combined with model parameter fitting and recommendation, so that end-users only have to transfer the recommended parameters into their applications to implement a tested model with a defined reliability over all known measurement data points. In the following, a survey on the existing and still maintained collections and databases on solutions is given.

4.4
Examples of Databases for Thermophysical Properties

Due to the fact that dozens of sources for thermodynamic data are now available on the Web, only a few major providers will be mentioned in this chapter. To have access to a larger overview about what is available on the Web, a look at the pages, e.g., of the University of Illinois should be considered (http://tigger.uic.edu/~mansoori/Thermodynamic.Data.and.Property-html).

A few examples for the largest and most famous databases are shown in Table 4.2. Three examples of databases are described as follows.

Table 4.2 Provider list for thermophysical data

Producer	Database name	URL
DECHEMA	DETHERM	www.dechema.de/detherm-lang-en.html
DDBST	DDB	www.ddbst.de/new/Default.htm
NIST	Properties of fluids	http://properties.nist.gov/
NIST	Chemistry WebBook	http://webbook.nist.gov/chemistry/
IUPAC-NIST	Solubility Database	http://srdata.nist.gov/solubility/
K&K Associates	Thermal Resource Center	www.tak2000.com/
FIZ Chemie	INFOTHERM	www.fiz-chemie.de
CERAM Research limited	Thermophysical Properties Database	www.ceram.co.uk/thermet.html
API	Technical database	www.dnv.com/software/all/api/index.asp
MDL	CrossFire Beilstein	www.mdl.com/products/knowledge/crossfire-beilstein/
TPC, Academy of Science Russia	THERMAL	www.chem.ac.ru/Chemistry/Databases/THERMAL.en.html
AIChE	DIPPR	http://dippr.byu.edu/
G&P Engineering Software	MIXPROPS	www.gpengineeringsoft.com/pages/pdtmixprops.html
G&P Engineering Software	PHYPROPS	www.gpengineeringsoft.com/pages/pdtphysprops.html
Ecole Polytechnique de Montreal	FACT	www.crct.polymtl.ca/fact/index.php
S. Ohe	Fundamental Physical Properties	http://data-books.com/bussei-e/bs-index.html
Prode	Prode Properties	www.prode.com/en/ppp.htm
NEL	PPDS	www.ppds.co.uk/Products/
THERMODATA	THERMODATA	http://thermodata.online.fr
Chinese Academy of Science	Engineering Chemistry Database	http://chinweb.ipe.ac.cn/

4.4.1 NIST Chemistry WebBook

The NIST Chemistry WebBook provides access to data compiled and distributed by NIST under the Standard Reference Data Program [5].

The NIST Chemistry WebBook [6] contains:

- thermochemical data for over 7000 organic and small inorganic compounds:
  - enthalpy of formation
  - enthalpy of combustion
  - heat capacity
  - entropy
  - phase transition enthalpies and temperatures
  - vapor pressure
- reaction thermochemistry data for over 8000 reactions:
  - enthalpy of reaction
  - free energy of reaction
- IR spectra for over 16,000 compounds;
- mass spectra for over 15,000 compounds;
- UV/V is spectra for over 1600 compounds;
- electronic and vibrational spectra for over 4500 compounds;
- constants of diatomic molecules (spectroscopic data) for over 600 compounds;
- ion energetics data for over 16,000 compounds:
  - ionization energy
  - appearance energy
  - electron affinity
  - proton affinity
  - gas basicity
  - cluster ion binding energies
- thermophysical property data for 34 fluids:
  - density, specific volume
  - heat capacity at constant pressure (C_p)
  - heat capacity at constant volume (C_v)
  - enthalpy
  - internal energy
  - entropy
  - viscosity
  - thermal conductivity
  - Joule-Thomson coefficient
  - surface tension (saturation curve only)
  - sound speed.

Data on specific compounds in the Chemistry WebBook based on name, chemical formula, CAS registry number, molecular weight, chemical structure, or selected ion energetics and spectral properties can be searched for.

4.4.2 DETHERM

The DETHERM [7] database provides thermophysical property data for about 24,000 pure compounds and 146,000 mixtures. DETHERM contains literature values, together with bibliographical information, descriptors and abstracts. At the time 5.2 million data sets are stored. DETHERM is a collection of data packages produced by well known providers of thermophysical packages, unified under a common graphical user interface. The database files in Table 4.3 are part of DETHERM.

An example for the actual possibilities for presentation of the results is seen in Fig. 4.1.

Table 4.3 Content of DETHERM

Dortmunder Datenbank DDB	**Phase equilibrium data**
(Prof. Gmehling, University of Oldenburg)	• Vapor-liquid equilibria • Liquid-liquid equilibria • Vapor-liquid equilibria of low boiling substances • Activity coefficients at infinite dilution • Gas solubilities • Solid-liquid equilibria • Azeotropic data Excess properties • Excess enthalpies • Excess heat capacities • Excess volume Pure component properties • Transport properties • Vapor pressures • Critical cata • Melting points • Densities • Caloric properties • Others
Electrolyte data collection ELDAR *(Prof. Barthel, University of Regensburg, LS Chemie IV)*	Caloric data Electrochemical properties Phase equilibrium data PVT properties Transport properties
Thermophysical database INFOTHERM *(FIZ CHEMIE)*	PVT data Transport properties Surface properties Caloric properties Phase equilibrium data • Vapor-liquid equilibria • Gas-liquid equilibria • Liquid-liquid equilibria • Solid-liquid equilibria Pure component basic data

Table 4.3 Content of DETHERM (Fortsetzung)

Dortmunder Datenbank DDB	**Phase equilibrium data**
Thermophysical Parameter Database	Phase equilibria
COMDOR *(Leuna GmbH in Cooperation with FIZ Chemie)*	Excess enthalpies Transport and surface properties Caloric and acoustic data
Data Collection C-DATA *(Institut for Chemical Technic, Prag)*	Twenty physicochemical properties for 593 pure components
Basic Database Böhlen BDBB *(Sächsische Olefinwerke AG Böhlen, now DOW Chemical)*	Pure component database of the Sächsische Olefinwerke with chemical and physical basic data for 1126 pure substances (mainly for the fields of petroleum and coal chemistry)
Additional *(DECHEMA e.V.)*	Vapor pressures Transport properties • Thermal conductivities • Viscosities Caloric properties PVT data • PVT data • Critical data Eutectic data Solubilities Diffusion coefficients

4.4.3 DIPPR Database [1]

The major content of the database of the Design Institute for Physical Property Data (DIPPR), a subsidiary of the American Institute of Chemical Engineers (AIChE) [8], are mainly data collections of pure component properties but also data for selected properties of mixtures and the results of a project related to environmental, safety and health data. In total data of 1700 compounds in the database cover mainly the components of primary interest to the process industries. The special focus of the DIPPR database is to provide reliable data of thermophysical properties, including the temperature dependency of the properties, which are approved by technical committees, where industrial experts are involved in the design of the database and in the evaluation of the data.

Table 4.4 gives an overview of the content of the DIPPR database.

The use of these databases is meanwhile a standard option in the preparation of the process design. A bigger difficulty is the absence of thermophysical data for newer processes involving electrolytes and of solutions containing biomaterial. This specific topic will be explained in the next chapter.

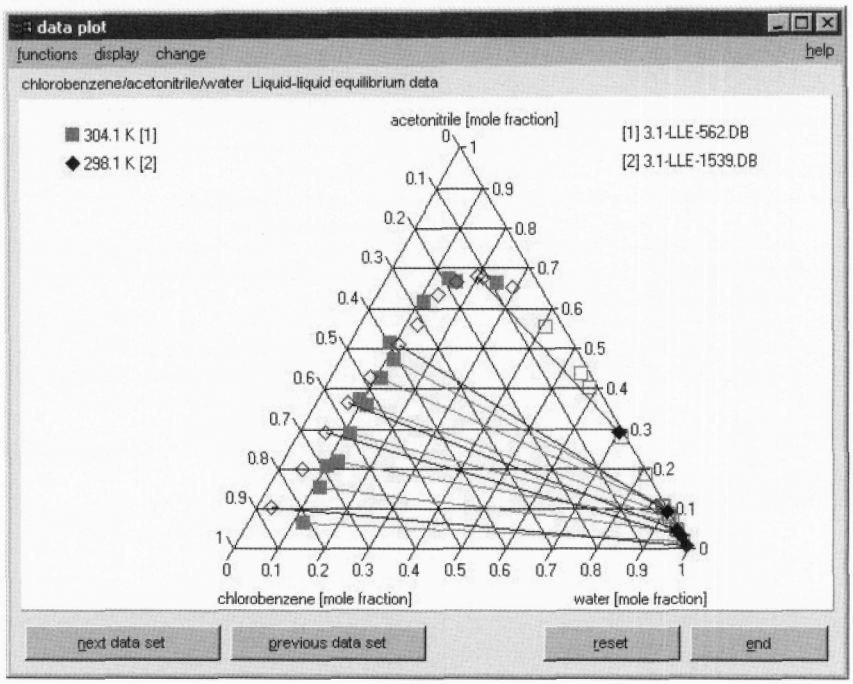

Figure 4.1 Joint graphical display of two different LLE data sets in DETHERM for the system chlorobenzene/acetonitrile/water

Table 4.4 Properties in the DIPPR 801 Database [9]

Constant properties: property	Units
Acentric factor	-
Auto ignition temperature	K
Dipole moment	C m
Absolute entropy of ideal gas at 298.15 K and 1 bar	J (kmol K)$^{-1}$
Lower flammability limit temperature	K
Upper flammability limit temperature	K
Lower flammability limit percent	Vol % in air
Upper flammability limit percent	Vol % in air
Flash point	K
Gibbs energy of formation for ideal gas at 298.15 K and 1 bar	J kmol^{-1}
Standard state Gibbs energy of formation at 298.15 K and 1 bar	J kmol^{-1}

Table 4.4 Properties in the DIPPR 801 Database [9] (Fortsetzung)

Constant properties: property	**Units**
Net standard state enthalpy of combustion at 298.15 K	J $kmol^{-1}$
Enthalpy of formation for ideal gas at 298.15 K	J $kmol^{-1}$
Enthalpy of fusion at melting point	J $kmol^{-1}$
Standard state enthalpy of formation at 298.15 K and 1 bar	J $kmol^{-1}$
Heat of sublimation	J $kmol^{-1}$
Liquid molar volume at 298.15 K	m^3 $kmol^{-1}$
Melting point at 1 atm	K
Molecular weight	kg $kmol^{-1}$
Normal boiling point	K
Parachor	–
Critical pressure	Pa
Radius of gyration	m
Refractive index	–
Solubility parameter at 298.15 K	$(J\ m^{-3})^{1/2}$
Standard state absolute entropy at 298.15 K and 1 bar	J $(kmol\ K)^{-1}$
Critical temperature	K
Triple point pressure	Pa
Triple point temperature	K
Critical volume	m^3 $kmol^{-1}$
van der Waals area	m^2 $kmol^{-1}$
van der Waals reduced volume	m^3 $kmol^{-1}$
Critical compressibility factor	–
Temperature-dependent properties: property	**Units**
Heat capacity of ideal gas	J $(kmol\ K)^{-1}$
Heat capacity of liquid	J $(kmol\ K)^{-1}$
Heat capacity of solid	J $(kmol\ K)^{-1}$
Heat of vaporization	J $kmol^{-1}$

Table 4.4 Properties in the DIPPR 801 Database [9] (Fortsetzung)

Temperature-dependent properties: property	Units
Liquid density	kmol m^{-3}
Second virial coefficient	m^3 $kmol^{-1}$
Solid density	kmol m^{-3}
Surface tension	N m^{-1}
Thermal conductivity of liquid	W $(m\ K)^{-1}$
Thermal conductivity of solid	W $(m\ K)^{-1}$
Thermal conductivity of vapor	W $(m\ K)^{-1}$
Vapor pressure of liquid	Pa
Vapor pressure of solid or sublimation pressure	Pa
Viscosity of liquid	Pa s
Viscosity of vapor	Pa s

4.5 Special Case and New Challenge: Data of Electrolyte Solutions

A much bigger challenge than these normal solutions is the modeling of electrolyte containing solutions. The modeling of electrolyte solutions or, more generally speaking, liquids containing fractions of electrolytes is nowadays still an exhausting task. Chemical and process engineers for example are nowadays able to model or even predict a vapor-liquid equilibrium, the density or viscosity of a multicomponent mixture containing numerous different species with sufficient reliability. But if only traces of salt are contained in the mixture, nearly all models tend to fail. The modeling results however have a great impact on the design and construction of single chemical apparatus as well as whole plants or production lines. Proper functioning could only be guaranteed based on reliable results.

Another area influenced greatly by electrolyte modeling is biochemical engineering. For example nobody knows how to predict quantitatively salting-out effect of proteins, crystallization processes of biomolecules, the influence of ions on nanoparticle formation, their size morphology and crystal structure, zeolite synthesis and so on. But the development of new production processes in this intensively growing area requires accurate macroscopic physical property models capturing accurately the underlying physics. In some cases there is a limited understanding of these mechanisms, but no real predictability.

The chemical engineer developing new production processes as well as the physical chemist developing models are therefore having a pressing need to access reliable

thermophysical property data. Process as well as model development, either predicting or even only interpolating, requires multitudinous amounts of reliable thermophysical property data for electrolytes and electrolyte solutions. Among the most important property types are:

- vapor-liquid equilibrium data
- activity coefficients
- osmotic coefficients
- electrolyte and ionic conductivities
- transference numbers
- viscosities
- densities
- frequency dependent permittivity data.

How does one find such data?

4.5.1
Reliable Data Sources

Thermophysical property data for electrolytes and electrolyte solutions are measured from numerous researchers and scientists and are published typically in a large number of journals and publications. But people requiring such data will not search the primary publications, because this is too time-consuming. And in most cases it is even impossible, because industrial users do not have access to all the required literature immediately. Instead the preferred way will be to check either a printed data collection or to search within an electronic database for the components, mixtures and properties one needs.

Such printed data collections or databases are typically compiled and/or maintained by individuals or groups having a well known reputation in that field. Therefore they have an overview of the primary literature publishing physical property data and are able to continuously add new data to their collections. In most cases these groups also use their own collections for model development. In the following pages, a survey of maintained databases for electrolyte properties is given.

4.6
Examples of Databases with Properties of Electrolyte Solutions

4.6.1
The ELDAR Database [10]

The Electrolyte Database Regensburg ELDAR is a numerical property database for electrolytes and electrolyte solutions. It contains data on pure substances and aqueous as well as organic solutions. The data collection for ELDAR started in 1976 within the framework of the DECHEMA study [11] *Research and Development for Sav-*

ing the Raw Material Supply which was supported by the German Ministry for Research and Technology (BMFT). The work of this study 1981 led to development of ELDAR. From the beginning up to now the ELDAR database development was headed by the Institute of Physical and Theoretical Chemistry of the University of Regensburg. The database was designed as a literature reference, numerical data and also model database for fundamental electrochemical research, applied research and also the design of production processes.

The database is still maintained and has roughly doubled its size since beginning. It contains data of more than 2000 electrolytes in more than 750 different solvents. Nowadays ELDAR contains approximately:

- 7400 literature references
- 45,400 data tables
- 595,000 data points.

ELDAR contains data on physical properties like densities, dielectricity coefficients, thermal expansion, compressibility, PVT data, state diagrams, critical data, thermodynamic properties like solvation and dilution heats, phase transition values (enthalpies, entropies, Gibbs free energies), phase equilibrium data, solubility, vapor pressures, solvation data, standard and reference values, activities and activity coefficients , excess values, osmotic coefficients, specific heats, partial molar values, apparent partial molar values and transport properties like electrical conductivities, transference numbers, single ion conductivities, viscosities, thermal conductivities and diffusion coefficients.

ELDAR is distributed as part of DECHEMA's numerical database for thermophysical property data, which is called DETHERM. To access ELDAR one could therefore use several options:

- in-house client-server installation as part of the DETHERM database [7];
- Internet access using DETHERM ... on the WEB [7];
- on-line access using host STN International [12].

To get an overview of the data available, the Internet access option could be recommended, because existence of data for a specific problem could be checked free of charge and even without registration.

4.6.2 The Electrolyte Data Collection

The Electrolyte Data Collection is a printed publication which is part of DECHEMA's Chemistry Data Series. The Electrolyte Data Collection is published by Barthel and his coworkers from the University of Regensburg. The printed collection and the database ELDAR have complementary functions. The data books give a clear arrangement of selected recommended data for each property of an electrolyte solution. The electrolyte solutions are classified according to their solvents and solvent mixtures. All solution properties have been recalculated from the original measured

data with the help of compatible property equations. A typical page of the books contains the following for the described system:

- general solute and solvent parameters
- fitted model parameter values
- measured data together with deviations against the fit
- a plot
- literature references.

The Electrolyte Data Collection has nowadays 18 volumes and consists of 9500 printed pages. Covered properties are:

- conductivities
- transference numbers
- limiting ionic conductivities
- dielectric properties of water, aqueous and nonaqueous electrolyte solutions
- viscosities of aqueous and nonaqueous electrolyte solutions.

4.6.3
ICV-SEP Data Bank for Electrolyte Solutions

The Engineering Research Center Phase Equilibria and Separation Processes (ICV-SEP) of the Technical University of Denmark (DTU) is operating a data bank for electrolyte solutions [13]. It is a collection of scientific papers containing experimental data for aqueous solutions of electrolytes and/or nonelectrolytes and also theoretical papers related to electrolyte solutions. The database is a mixture between a literature reference database and a numerical database. Currently references to more than 4000 papers are stored in the database. In addition experimental data from around 2000 of these papers are stored electronically as well. Most of the experimental data concern aqueous solutions. The access to the literature reference database is free of charge, but requires a registration. The access to the numerical database is restricted to members of an industrial consortium supporting the work of ICV-SEP.

4.6.4
The Dortmund Database DDB [14]

The Dortmund Database Software and Separation Technology from the University of Oldenburg is well known for its data collections in the areas of vapor-liquid equilibria and related properties. While the major part of the data collections is dealing with nonelectrolyte systems, two collections contain exclusively electrolyte data. They are focused on:

- vapor-liquid equilibria
- gas solubilities.

The two collections together currently contain 3250 data sets. Access to these collections is possible either on-line using the DETHERM on the Web or in-house using special software from DDBST or DECHEMA.

4.6.5
Closed Collections

In addition to the above-described publicly available and still maintained collections, do other old electrolyte data collections exist? Among them is for example the ELYS database, which was compiled by Lobo, Department of Chemistry, University of Coimbra, Portugal, or the DIPPR 861 Electrolyte Database Project. But these closed collections are typically not maintained any more and also not publicly available. It is likely the references and/or data published in these collections could also be found inside the aforementioned living collections.

4.7
A Glance at the Future of the Properties Databases

Most of the engineers in chemical companies trust in the power of their evaluation of the equations of state for the calculation of the optimal point of work. Nevertheless the opinion that databases have less importance these days is growing, mainly when budgetary elements come into consideration. The knowledge of the importance of a correct process design is run over by considerations that a saving of one euro per kg for a product which costs 50 euros per kg is not very relevant. That is not the case for basic chemicals, where saving of the same order of magnitude represents 25 % of the total costs and 10 % of the used energy. Unfortunately the production of these chemicals is today mainly transferred into low cost countries, i.e., not very relevant for research purposes. A lot of companies made the outsourcing of their measurements, so that only a limited amount of experts in companies maintain the knowledge for these activities.

When we look at the constraints to find new methods for the design of biologic or polymer solutions, we must be sceptical to find enough people to manage future visions for models with the knowledge what was in the past. In the time of a rise in steel consumption in the Chinese industry, where in an unexpected way a demand of coal energy started again, it may be that the properties will rise in interest. From a governmental funding point of view, it is a good sign that new projects are coming up in order to find a new approach to build evaluated databases.

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