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# Experimental Datasets from Chemical Thermodynamics

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## Content



I have been working for quite awhile with the treatment of experimental results in chemical thermodynamics. I have tried to organize my archives and make them available for others. There are

several experimental datasets in computer readable format and I hope that they can be used as useful benchmarks for data fitting and nonlinear optimization. Experimental values have been collected from original research papers describing experimental results. All case studies are reasonably well documented in my papers. As such, the goal of the current document is to collect related information together.

# Problem

The problem is essentially usual data fitting. There are some observations and the goal is to find a set of unknown parameters for some phenomenological model. For example, parameter estimates can be found by minimizing the sum of squared residuals and this leads to a nonlinear optimization problem.

Chemical thermodynamics adds several interesting features. In chemical thermodynamics, parameterization is done at the level of the master function (the Gibbs energy) yet experimentally measured quantities are not related to it directly. Instead there are two different classes of experiments. First one can measure thermodynamics properties, that can be expressed as the first or second derivatives of the Gibbs energy. Second one can measure phase equilibria (phase diagrams) that can be expressed by equating chemical potentials (a system of nonlinear equations). As a result:

- A dataset comprises several heterogeneous experiments. This means that an observation may mean completely different physical quantities possessing different physical units in different experiments.
- The difference between different experiments is greater than the reproducibility error because, as one could expect, there are inevitable systematic errors.
- Sometimes, computation of a residual cannot be done analytically but instead requires a numerical solution of another numerical problem by itself. For example, solution of a nonlinear system of equations for phase equilibria. An additional problem is that for an arbitrary point in the parameter space, this additional numerical problem may not have a solution at all.

More information:

- TDLIB manual [1]. See Section 2.3 for a data fitting problem in chemical thermodynamics and Sections 2.1 and 2.2 for a thermodynamic problem by itself.
- Section Thermodynamic model in [2] as an example of a typical model in chemical thermodynamics.
- Ref [3] describes my approach based on variance component analysis to treat systematic errors.

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# Experimental Datasets

## File Format

Experimental values are written in a plain ASCII file in the free format. White space is recognized as a delimiter. The file consists from experiments separated by semicolon. Each experiment comprises following fields separated by commas

```
experiment_ID,
equation_ID,
variables_names,
point1,
point2,
...;
```

`experiment_ID` is the experiment name and `equation_ID` is the equation name to treat the experimental points. The reference to the original work as well as the meaning of `equation_ID` can be found in the corresponding paper. The same `equation_ID` can be used for several experiments. `variables_names` are two or more identifiers separated by space. The number of names in `variables_names` is equal to number of numerical values in the experimental point. Usually the first name means what has been measured and the second name what has been controlled. `point1` contain numerical values separated by space. The number of numerical values is equal to the number of words in `variables_names`.

Information written after the first word in `experiment_ID` and `equation_ID` is considered to be a comment. The information in `pointN` after the number of numerical values equal to that in `variables_names` is also considered to be a comment.

Not all experiments and experimental points from the file have been taken into consideration. Symbol * before `experiment_ID` shows that this experiment has been discarded. Symbol * before `pointN` shows that this experimental point has been discarded.

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## Vaporization of KCl

In the vapors of KCl, there are monomer and dimer molecules. Total vapor pressure, Knudsen effusion and transpiration methods have been used to determine experimentally thermodynamics of the KCl vaporization. The measured values are tied with the enthalpies and entropies of two independent vaporization reactions. The thermodynamic model as well as available experimental results are described in Ref [4] ([5] is an extended version of [4] in English). The discussion of the data treatment is also included in [3].

The dataset kcl.dat includes 460 experimental points measured in 29 different experiments from 25 research papers. The file kcltotal.dat (in slightly different format) also includes results from 8 additional works that has been discarded by us at the preliminary stage (see [4] or [5]).

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## *The Ba-Cu System*

The Ba-Cu phase diagram includes melt and two intermetallic phases. The Gibbs energies of the phases have been parametrized and unknowns have been found by joint processing of heterogenous experimental results: the heat of mixing, the heat of formation and points from the phase diagram. The thermodynamic model and experimental results are described in [2] and [6].

The dataset bacu.dat includes 178 experimental points measured in 18 different experiments from 5 research papers.

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## *The Cu-Y System*

The Cu-Y phase diagram includes melt and five intermetallic phases. The Gibbs energies of the phases have been parametrized and unknowns have been found by joint processing of heterogenous experimental results: the heat of mixing, the heat of formation and points from the phase diagram. The thermodynamic model and experimental results are described in [2] and [7].

The dataset cuy.dat includes 185 experimental points measured in 35 different experiments from 12 research papers.

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## *Thermodynamics of Calcium Aluminates*

There are four calcium aluminates. Their enthalpy of formation and entropies have been determined during simultaneous processing of the calorimetry and electrochemistry experimental values. The thermodynamic model and experimental results are described in [8].

The dataset emf.dat includes 165 experimental points measured in 21 different experiments from 8 research papers.

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## *Thermodynamics of $YBa_2Cu_3O_{6+z}$ (Y123)*

The $YBa_2Cu_3O_{6+z}$ phase (Y123) is the first high temperature superconductor. Note that the term "high temperature" is always relative. After the discovery of superconductive properties of Y123, there was a lot of research around the world. The model for the Gibbs energy has been suggested by Voronin and Degterov. Note that the Gibbs energy by itself cannot be computed analytically and it is necessary to solve a small numerical problem to compute G(T, p, z) each time. The thermodynamic model and experimental results are described in [9].

The dataset y123.dat includes 2109 experimental points measured in 179 different experiments from 57 research papers.

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# References

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**Computational Thermodynamics Library,** TDLIB'00, 2000.
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**Thermodynamic assessment of the Ba-Cu system**.
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[8]*V. V. Kuzmenko, I. A. Uspenskaya, E. B. Rudnyi*.
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[9]*E. B. Rudnyi, V. V. Kuzmenko, G. V. Voronin*.
**Simultaneous assessment of the $YBa_2Cu_3O_{6+z}$ thermodynamics under the linear error model**.
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