New thermodynamic database and software for the applied chemistry and materials science

Voskov A.L., Uspenskaya I.A.
Introduction

Our previous experience

• PhDi program (binary phase diagrams)
• TernAPI program (ternary phase diagrams)
• CpFit program (arbitrary heat capacity models parameters optimization)

The aim of this work is development of the consistent framework for CALPHAD approach (calculation of phase diagrams, thermodynamic models optimization etc.)
Software structure

Interface:
GUI, Console, API

Models parameters optimization

Equilbria calculation methods
- Convex hulls
- Equilibrium constants
- G min.search

Database
- Models parameters
- Experimental data
- Bibliography

Interface:
Qt 5.x

Software:
- Ceres solver
  - Ceres Solver
  - qhull

Interface:
Lua 5.x
Advantages of Lua programming language:

- Support of arbitrary functions
- Support of complex data structure
- Human-readable format
- Allows inline data conversion, writing scripts for conversion from other data formats

```lua
out = {
    attr = "DIR",
    acids = {
        HCl = {
            beta = {0.18024, 0.27154},
            alpha = {2.0},
            Cphi = {0.00006},
            Cphi_alpha = {}
        },
        HBr = {
            beta = {0.19622, 0.34529},
            alpha = {2.0},
        }
    },
}
```
Heat capacity (and other thermodynamic functions) are approximated by sum of Einstein-Planck functions, i.e.:

\[
C_p(T) = \sum_i \alpha_i C_E \left(\frac{\theta_i}{T}\right); \quad \frac{C_E(x)}{R} = \frac{3x^2 e^x}{(e^x-1)^2}
\]

\[
H(T) - H(0) = \int_0^T C_p(T) dT = \sum_i \alpha_i \left[U_E \left(\frac{\theta_i}{T}\right) - U_0\right]
\]

\[
S(T) - S(0) = \int_0^T \frac{C_p(T)}{T} dT = \sum_i \alpha_i S_E \left(\frac{\theta_i}{T}\right)
\]

\[
\frac{S_E(x)}{R} = 3 \left[\frac{x}{e^x-1} - \ln(1 - e^{-x})\right]; \quad \frac{U_E(x) - U_0}{RT} = \frac{3x}{e^x-1}
\]

Note: number of terms and \(\alpha_i, \theta_i\) values are found by the least squares method (using experimental data)

The least squares method

\[ RSS = \sum_{i=1}^{n} \omega_i^2 (Y_{i}^{calc} - Y_{i}^{exp})^2 \]

*RSS* = residual sum of squares (to be minimized)

\( Y = C_p \) or \( H \) values (experimental or calculated)

\( \omega_i = \omega_i^0 \) statistical weight for absolute deviations

\( \omega_i = \omega_i^0 / Y_{i}^{exp} \) statistical weight for relative deviations

**Statistical significance of \( \alpha_i \) and \( \theta_i \) coefficients**

\[ \Delta \beta = t_{\alpha,f} \hat{\sigma} \sqrt{\text{diag} (J^T J)^{-1}}; \quad \hat{\sigma}^2 = \frac{RSS}{f}; \quad J_{ij} = \omega_i \left( \frac{\partial Y_{i}^{calc}}{\partial \beta_j} \right) \]

\( \beta \) – model parameters, \( \Delta \beta \) – confidence intervals

\( J \) – Jacobian, \( t_{\alpha,f} \) - t-distribution two-sided quantile

Lourakis M.I.A. LEVMAR library [http://www.ics.forth.gr/~lourakis/levmar/]
Examples: database
Example: ThO$_2$

Requires 5 Einstein-Planck function terms for non-anomalous part
Example: Tl-substituted natrolite

\[ \text{Tl}_{1.87}\text{Na}_{0.05}\text{Mg}_{0.03}[\text{Al}_{1.98}\text{Si}_{3.02}\text{O}_{10}] \cdot 2.33\text{H}_2\text{O} \]

The database contains 46 zeolites

Convex hull method

A subset $S \subseteq \mathbb{R}^3$ is convex if for any two points $p$ and $q$ in the set the line segment with endpoints $p$ and $q$ is contained in $S$. The convex hull of a set $S$ is the smallest convex set containing $S$.

Convex hull of Gibbs energies of all phases = equilibrium G surface
Convex hull method

1. Gibbs energies of phases

2. Convex hull

3. Convex hull projection

4. Phase diagram
Examples: binary systems
Examples: ternary systems (TernAPI engine)

\[ G = -TS^{id} + L \left[ \sum_{i<j} x_i x_j (x_i - x_j)^2 + 2.5x_1x_2x_3 \right] \]

\[ L = 20 \text{kJ/mol} \]

\[ T = 1423 \text{K} \]
Examples: electrolytes aqueous solutions
Thank you for your attention!