Thermodynamic database development based on ab initio calculations: challenges and opportunities

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Outline

• Thermodynamic database content
• Database development
  – Based on experiments
  – Based on ab initio
• Challenges
• Opportunities
Thermodynamic database content

- $\Delta H^{298}$
- $S^{298}$
- $C_p(T)$, $G(T)$
- $\mu$
- $T_C$
Thermodynamic database content

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- $S^{298}$
- $C_p(T)$
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- $\mu$
- $T_C$
- $\rho$
- $\alpha(T)$
- $\kappa(T)$
- $B'(T)$
Thermodynamic database content

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- $S^{298}$
- $C_p(T)$
- $\mu$
- $T_c$
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- $\kappa(T)$
- $B'(T)$
- $L(T)$
- $G(T, p)$
- $G(T, p, X_i)$
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Database development based on experiment

• Ideal: The following properties are measured:
  – binary phase diagram
  – enthalpies of (trans-)formation of the compounds
  – enthalpies of mixing and constituent activities of solutions as f(T)
  – heat capacities of compounds and solutions
  – crystal structures, especially for complex solutions
  – density as f(T)
  – elastic properties as f(T)

• Real: Few of the properties are measured.
Database development based on experiment

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  Thermodynamic properties are fitted to all available measurements
Database development based on experiment

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2nd step: Consistency checks of binary and ternary systems!

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→ materialsproject.org, oqmd.org, aflowlib.org, nomad-coe.eu
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Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

Publications including “lattice stability”
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Publications including “lattice stability”

- Kaufman et al. (1963), Lattice Stability of metals .3. Iron
- Dinsdale (1991), SGTE data for pure elements
- Wang et al. (2004), Ab initio lattice stability in comparison with CALPHAD lattice stability
- Kirklin et al. (2015), The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies
Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

Raw data:

$\Delta H_{f,\text{OQMD}} - \Delta H_{f,\text{SGTE}}$ [eV/atom]

Mean average error is $\sim 13$ kJ/mol atoms

Kirklin et al. (2015), The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies

(1 eV/atom $\approx 100$ kJ/mol atoms)
Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

Linear correction for elements:

Kirklin et al. (2015), The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies

(1 eV/atom ≈ 100 kJ/mol atoms)

$\Delta H_{f,\text{OQMD}} - \Delta H_{f,\text{SGTE}}$ [eV/atom]

Mean average error is ~9 kJ/mol atoms
Challenge: \( \Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}} \)

**WHY?**

Linear correction for elements:

- Iodides
- Bromides
- Oxides
Challenge: “High“ temperatures
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Ab initio calculations are mostly done at 0K.
How to extrapolate to room temperature and above?
→ Einstein model
→ Debye model
  → $\propto C_p = \text{const}$
→ Other models for $T > \theta_D$ are computationally expensive!

FCC-Al: $\theta_D = 267$ K
Challenge: Liquid and gas phases

• There is currently no high-throughput solution in ab initio calculations…
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Opportunities: Unstable allotropes

Different allotropes are often modelled with the same $C_p(T)$-function.
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There is an excellent agreement of $C_p,\text{FCC-Al}$ between SGTE and ab initio calculations at $298 \, \text{K} \approx \theta_D (=267\,\text{K})$.

$C_p,\text{BCC-Al}$ should be slightly higher!
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$C_p,BCC-Al$ should be slightly higher!

There is a disagreement of $S,FCC-Al$ between SGTE and ab initio calculations at 298 K.

Ab initio calculations can help improving properties that are hard to measure!
Opportunities: Enthalpies at low $T$

- It is impossible to measure enthalpies at low temperatures due to kinetic constraints.

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“The predicted critical temperature is very close to the lower limit of the temperature range of currently known experimental phase diagrams.”

Opportunities: Navigating Chemical Compound Space

Today: SGTE Solution database contains ~1500 phases. That allows description of

- 577 binary systems,
- 141 ternary systems,
- 15 higher order systems
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~70 non-radioactive, non-noble gas elements

\[ 70 \times 69 = 4830 \text{ binary systems} \]
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Thank you very much for your attention!