An attempt to document the status of the third generation unary database project for all interested

Bo Sundman March 30, 2021

1 Introduction

This is an dynamic summary to keep everyone involved updated with the current development of the 3rd generation of the Calphad unary database. It also contains unresolved issues and ongoing discussions in Appendices.

The aim is to make the new thermodynamic databases closer to the physical reality while **keeping them useful for demanding engineering applications which need rapid calculation of equilibria and various thermodynamic properties in multicomponent systems.** The current unary database using the 1991 SGTE unary database by Dinsdale [7] will continue to be used in parallel for the foreseeable future.

Section 2 is a very short summary of decisions and unresolved issues, usually with a short motivation. We should keep this short and use the Appendices for detailed explanations, expressing different opinions and discussions.

At present the Appendices are mainly my personal view of things, but everyone should express their opinions there. All mistakes should also be recorded, otherwise we will make the same mistakes over and over again.

2 Executive summary of sub projects

The sub projects are closely related, not independent.

1. **Heat capacity zero at $T = 0$,** for details see Appendix B.

   This is a mandatory physical reality.

   (a) The Einstein model, is used to describe the low T heat capacity of all phases, stable or metastable. The Einstein model is preferred because it can easily be integrated to a Gibbs energy and even using a Debye model an additional polynomial in T is needed to fit experimental data.

   (b) The additional polynomial in T must not have any terms in T with powers ≤ 1 or $T\ln(T)$ and should not have any breakpoints.

   (c) The Einstein model has a parameter, denoted θ, which is related to the phonon frequencies of the element. To fit the heat capacity of a pure element, stoichiometric phase or an endmember of a solution phase, a sum of several Einstein functions with different θ and weight factors can be used. Normally the weight factors should sum up to unity (or the number of atoms involved).
   (d) In a solution phase θ will vary with composition. For simplicity each element should have a single θ selected to vary with composition, see Appendix B.1.

2. **Entropy zero at $T = 0$,** for details see Appendix C.

   (a) The entropy of perfect crystalline phases at $T = 0$ K must be zero according to the third law. This means there must not be any Gibbs energy parameters with terms depending on T with power ≤ 1.
   (b) The amorphous phase and crystalline phases that are not perfectly ordered at $T = 0$ K (for example magnetite) can have a positive entropy at $T = 0$ K, The opinion of Göran Grimvall is explained in Appendix C.
   (c) Excess Gibbs energies and other Gibbs energy parameters can have their linear T dependent coefficients, converted to an excess parameter for the θ parameter according to Dinsdale et al. [14]. See Appendix C.1.

3. **Model for magnetism**, for details see Appendix D.

   The models by Qing [9] and Xiong [10] are accepted with minor modifications. *Add some references of recent assessments!*

4. **Extrapolation of the heat capacity of liquids below their solidification T**, for details see Appendix E.

   The liquid two-state model proposed by Ågren [5] and recently described in Becker et al. [11] is used. A recent assessment of Al-C is by Zhangting et al. [16].

   This model describe the amorphous and liquid phases with a single Gibbs energy function.

   (a) The Gibbs energy of the stable liquid and its metastable extrapolation to low T is described by a single Gibbs energy function including a model parameter G^d_M.
   (b) The low T amorphous phase, G^{amf}_M, is described by an Einstein model and a polynomial as explained in section 1. There can also be a magnetic contribution [9].

   - (c) The transition from the amorphous to stable liquid (glas transition) as well as the stable liquid is described by a composition dependent G_M^d parameter with a polynomial in T.
   - (d) The polynomial for G_M^d may include terms with T and $T\ln(T)$ because G_M^d must be zero when extrapolated to low T.

5. **Extrapolation of the heat capacity of crystalline phases above their melting T,** for details see Appendix F

   The Equi-Entropy Criterion (EEC) proposed by Sundman et al. [15] is used to prevent the reappearance of crystalline solids extrapolated to high T. EEC replaces the breakpoint used in the SGTE 1991 unary database at the melting T of the solid phase of the pure elements by a software test of the entropy of solid and liquid phases. It has been used in the assessment by Zhangting et al. [16]

3 Some related topics

Modeling of thermal vacancies is discussed in Appendix G and molar volumes in Appendix H.

References

[1] Neumann, F. *Untersuchung über die spezifische Wärme von Minaralien*, Ann. Phys. Chem. 99 (1831) 1–39.

[2] Kopp, H. Über die spezifische Wärme der starren Körper, Ann. Chem. Pharmacie Suppl. 3 (1864) 289–342.

[3] Kaufmann, L and Bernstein, H *Computer calculation of phase diagrams*, (1970) Academic Press, New York, USA

[4] Hillert, M. *Some viewpoints on the use of a computer for calculating phase diagrams* Physica 103B **130B** (1981) 31-40

[5] Ågren J, *Thermodynamics of Suercooled Liquids and their Glass Transition* Phys. Chem. Liq, **18** (1988) 123-139

[6] Tallon, J.L. *A hierarchy of catastrophes as a succession of stability limits for the crystalline state*, Nature 342 (1989) 658–660.

[7] Dinsdale, A, *SGTE data for pure elements* Calphad **15** (1991) 317-425

[8] Sundman, B, *An assessment of the Fe-O system*, J Phase Equil. **12** (1991) 127-140

[9] Chen, Q et al., *Modeling of Thermodynamic Properties for BCC, FCC, Liquid and Amorphous Iron* J Phase Eq. **22** (2001) 631-644

[10] Xiong, W et al., *Magnetic phase diagram of the Fe-Ni system*, Acta Mat. **59** (2011) 521-530

[11] Becker C. A. at al., *Thermodynamic modelling of liquids: Calphad approaches and contributions from statistical physics* Phys. Stat. sol., (2014) doi:10.1002/pssb.201350149

[12] Rogal, J et al., *Perspectives on point defect thermodynamics* Phys. Stat. sol., (2014) doi:10.1002/pssb.201350155

[13] Wang, P, Xiong, W, Kattner, U.R., Campbell, C.E., Lass, E.A, Kontsevoi, O.Y, Olson, G.B, *Thermodynamic re-assessment of the Al-Co-W system* Calphad, **59**, (2014) 112-130

[14] Dinsdale, A et al. *Use of third generation data for elements to model the thermodynamics of binary alloy systems: Part I - The critival assessment of data for the Al-Zn system*, Calphad **68** (2020) 101723

[15] Sundman, B et al. *A method for handling the extrapolation of solid crystalline phases to temperatures far above their melting point*, Calphad **68** (2020) 101737

[16] Zhangting, H et al. *The third generation Calphad description of Al-C including revisions of pure Al and C*, Calphad **72** (2021) 102250

Appendix A The Gibbs energy per mole atom or formula unit

A model for the physical contribution to the Gibbs energy, ${}^{\mathrm{phy}}G_m$, is normally per mole atoms indicated by the subscript m. However, the Gibbs energy models based on the compound energy formalism (CEF) [4], require the contribution per mole formula units of the phase. CEF use formula units because many phases contain vacancies or more complex constituents than the pure elements. In such a case the physical model function must be multiplied with the number of atoms/formula unit of the phase α, M^α, calculated as:

$$M^\alpha = \sum_{\mathrm{A}} \sum_s a_s^\alpha \sum_i b_{i\mathrm{A}} y_{si}^\alpha \tag{A1}$$

$$^{\mathrm{phy}}G_M^\alpha = M^\alpha \cdot {}^{\mathrm{phy}}G_m^\alpha \tag{A2}$$

where A are the components, a_s is the number of sites on sublattice s, $b_{i\mathrm{A}}$ the stoichiometric factor of A in constituent i and y_{is} is the fractions of constituent i on sublattice s.

This fact has been ignored in earlier application of the magnetic model resulting in nonphysical values of the Bohr magneton number for some phases, for example in the assessment of magnetite by Sundman [8].

Appendix B The Einstein model at low T

Integrating the Einstein heat capacity model

$$C_P = 3R(\frac{\theta}{T})^2 \frac{\exp(\theta/T)}{(\exp(\theta/T)-1)^2} \tag{B1}$$

where θ is fitted to experimental data for the elements gives a Gibbs energy:

$$^{\mathrm{Ein}}G_m = 1.5R\theta + 3RT\ln(1-\exp(-\theta/T)) \tag{B2}$$

The Einstein model is preferred because it is simpler than any other model to integrate to a Gibbs energy. Even with a Debye model an additional polynomial in T is needed to describe the experimental data for each pure element.

The polynomial in T added to the Einstein function must not include terms with powers in $T \leq 1$ or $T\ln(T)$.

Note that θ depends on composition and possibly P but must not depend on T.

B.1 Modeling with multiple θ parameters

In some cases a pure element, stoichiometric compound or endmember has its heat capacity fitted using multiple θ, for example pure C as graphite. A predefined function, GEIN, with a single parameter, θ can be used in the Gibbs energy expression to calculate the contribution according to eq. B2, and its derivatives with respect to T.

The question is if these separate θ should be allowed to very with composition.

Bosses opinion:
To avoid complications in solutions a single θ should be selected for each element or endmember to model the composition dependence even if the element itself is described using several θ. The reason is that:

i) θ is an approximation of the phonon spectra,
ii) the heat capacity data for solutions are not well known and
iii) to avoid very complex modeling issues replacing linear T dependence in other Gibbs energy parameters by θ parameters.

To do anything better than a single θ in solutions we should model the phonon spectra which far outside the Calphad level of ambitions.

It is simple to select one θ, normally representing the major phononl frequency, as the composition dependent θ used in the explicit Einstein contribution with a composition dependent θ. This contribution must subsequently be subtracted from the Gibbs energy functions fitted with multiple θ for the element.

Appendix C The entropy at $T = 0$ K

Göran Grimvall sent me a few emails about the entropy at 0 K in August 2019 which I have summarized and translated below.

Here is a short summary of my opinions:

1. *Pure elements and stoichiometric compound without defects and which are dynamically stable has $S = 0$ when $T = 0$.*
2. *Amorphous structures have finite (positive) entropy at $T = 0$ K, see below.*
3. *Stoichiometric compounds with prefect structure but atomic disorder has finite entropy at $T = 0$ K (one can argue in the same way as for amorphous phases).*
4. *Phases that are dynamically unstable at certain T and/or composition has neither a defined entropy nor Gibbs energy. In Calphad one can assign them any value as long as it does not have any consequences for the stable system. But it is reasonable to treat them similarly to metastable phases using $S = 0$ at $T = 0$ K and have positive θ.*

For the amorphous phase:

Consider a big piece of an amorphous system. Cut a large but finite part of this with N atoms. Call this piece A and consider it as a perfectly ordered unit cell. If

A is repeated periodically we have a system with entropy 0 at $T = 0$ K. But we can also cut other parts in the big system, B, C, D etc all with N atoms. If any of these is repeated periodically we have a system with entropy 0 at $T = 0$ K. But this is not the case for an amorphous system. Instead it should be treated as a disordered system with parts A, B, C etc. This disorder means a finite entropy at $T = 0$ K. The larger value of N the greater number of alternative parts B, C etc.

Another way to argue: the entropy $S = k_B \ln(\Omega)$ is a measure of the degree of disorder, Ω, i.e. the number of separate subsystems A, B, C etc. with practically the same energy. If N is large then Ω is also large but the number of subsystems, A, B, C etc. with N atoms in a given part of a large amorphous sample varies with 1/N. Thus there is a given entropy per atom in an amorphous sample.

C.1 Converting linear T terms to Einstein θ

Following a proposal from Dinsdale et al. [7] to avoid non-zero entropy at 0 K means that any linear T terms in the classical Kaufman lattice stabilities [3] (and several later papers) can be converted to a $\Delta\theta$ for the metastable phase to avoid non-zero entropy in the metastable phases for the pure elements.

Linear T terms in excess parameters and other parameters contributing to the Gibbs energy can also be converted to a parameter in the composition dependence in θ. In principle a coefficient for a linear T term **"b"** can be replaced by **"b/3R"** in a θ parameter with the same composition dependence.

Some care should be used to avoid negative θ.

Appendix D The magnetic model

The contribution to the Gibbs energy due to the magnetic properties per mole atom is:

$$
\begin{aligned}
{}^{\mathrm{magn}}G_m &= RTf(\tau)\ln(\beta+1) && \text{(D1)}\\
\tau &= \frac{T}{T_C} && \text{(D2)}
\end{aligned}
$$

where T_C is the Curie or Neel T and β is the Bohr magneton number, all of which can vary with the composition. The magnetic contribution from eq. D1 is zero when either Curie or Neel T is negative.

NOTE the current functions [$f(\tau)$] etc. should be added.

The magnetic equation should be multiplied by M^α, see Appendix A, when used per mole formula unit.

There are separate Neel and Curie T and it is quite surprising to find that for a magnetic element the Neel and Curie T should have identical values but with opposite sign!

Individual Bohr magneton numbers for the elements is not adopted yet. The same Bohr magneton number is used for ferro- and antiferromagnetism as well as any kind of magnetic contribution.

...unfinished, some recent assessment references needed

Appendix E The liquid two-state model

The liquid phase is described using a two-state model described in Becker et al. [11].

This model has a Gibbs energy description including an Einstein heat capacity contribution for the metastable low T part of the liquid, G_M^{amf}, assumed to be an amorphous phase. It has also a parameter, G_M^d, describing both the transition to the liquid phase and the stable liquid above the melting T of the element:

$$G_M^{\mathrm{liq}} = G_M^{\mathrm{amf}} - RT\ln(1+\exp(-\frac{G_M^d}{RT})) \tag{E1}$$

As low T the term $\exp(-\frac{G_M^d}{RT})$ should approach zero and the second term in eq.E1 can be ignored. For the stable liquid $\exp(-\frac{G_M^d}{RT})$ should be much larger than unity and second term becomes:

$$\begin{aligned} -RT\ln(1+\exp(-\frac{G_M^d}{RT})) &\approx -RT\ln(\exp(-\frac{G_M^d}{RT})) = G_M^d && \text{(E2)} \\ G_M^{\mathrm{liq}} &= G_M^{\mathrm{amf}} + G_M^d && \text{(E3)} \end{aligned}$$

and thus the stable liquid is described by a sum the parameters in $G_M^{\mathrm{amf}} + G_M^d$.

In the G_M^{amf} parameter one can use a linear T term because the amorphous phase may have nonzero entropy at 0 K. But no $T\ln(T)$ and no T powers less than 1 because the amorphous phase must have zero heat capacity at $T = 0$ K.

In the G_M^d parameter both linear T and $T\ln(T)$ terms are possible because this should not give any contribution at low T.

The parameters for the liquid two-state model, G_M^d, can be very different for elements with different melting T, for example Al and W [13]. Great care should be taken determining parameters in G_M^d, Composition dependent parameters for the stable liquid can be used in both G^{d}_{M} and G^{amf}_{M} but usually very little is known about the amorphous phase. Interaction parameters in the G^{d}_{M} can have linear T and $T\ln(T)$ terms as they will not influence the low T properties.

Appendix F The equi-entropy criterion, EEC

The breakpoint at the melting T for the pure elements in the 1991 SGTE unary was an emergency fix to avoid that solid phases, which normally have an increasing heat capacity before melting, would become stable again when this increase is extrapolated to higher T. This will happen if the extrapolated heat capacity of the solid is larger than that of the liquid, which normally is fairly constant around $3R$. In the 1991 SGTE unary the heat capacity of the extrapolated solid was forced to approach that of the liquid above the breakpoint. The breakpoint represents a kind of 2nd order transition in the solid and it solved the primary problem but created others, for example strange heat capacity curves for compounds with their heat capacity modeled with the Neumann-Kopp rule [1, 2] and with higher melting T than a constituent element.

The similar breakpoint for the liquid, to avoid that the liquid becomes stable at low T, is removed by the liquid two-state model, see Appendix E. But there is no similar way to prevent the heat capacity of extrapolated solid to increase.

Instead a well established experience that **the liquid is always the condensed phase with the highest entropy in a system**, is used to prevent the extrapolated solid to become stable at high T. The liquid will have higher entropy than any stable solid phase in a system independently of the phase compositions.

The Equi-Entropy Criterion (EEC) proposed by Sundman et al. [15] is based on this experience. During an equilibrium calculation EEC will compare, at the same T, the entropy of the solid phases with the entropy of the liquid at their current compositions. If a solid phase is found to have higher entropy than the liquid the conclusion is that the solid suffers from a bad extrapolation of its heat capacity and the solid will not be allowed to be stable even if that would lower the Gibbs energy of the system.

EEC does not require any modification of the Gibbs energy expression of the solid extrapolation but must be implemented in the thermodynamic software using the data. No breakpoint is needed in the Gibbs energy function of the solid but some care should still be used to avoid that the heat capacity increases very rapidly above its melting T.

It is not forbidden to introduce a breakpoint in order to use the data in a software where EEC is not implemented but such a breakpoint should be at an even 100 K above the melting T, to indicate it is a fictitious breakpoint, and the derivative of the heat capacity should be continuous at the breakpoint to avoid the resemblance with a 2nd order transition.

During the discussions of EEC there were attempts to define a "crystalline breakdown T", which should be a few 100 K above the melting T but it was found difficult to handle for solution phases and abandoned. EEC is related to the "entropy catastrophe" criteria [6] for a pure compound but it is applied to cases when the solid and liquid does not have the same composition because at the same T no solid phase can exist with a higher entropy than the liquid.

Appendix G Thermal vacancies

All phases has defects of different kinds and the thermal vacancies are important for simulating kinetic properties. The Gibbs energy for thermal vacancies in a phase, G_{Va}, should be:

$$^{\circ}G_{\mathrm{Va}} \approx 2.3T \tag{G1}$$

according to Rogal et al. [12], in order to limit the maximal vacancy fraction to 10%.

There are several other proposals for thermal vacancies but it should be recognized that this energy is not related to vaporization or equilibrium with any other phase, most vacancies are created when atoms move to a grain boundary or other crystalline defect.

Appendix H Modeling the molar volume

The volume is not included in the 1991 unary database but is of great importance. Some ideas:

1. The most recent discussion made me think that the thermal expansion of elements should be zero at $T = 0$? Maybe use an Einstein function for α?

   $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{H1}$$

   possibly with the same θ as for the heat capacity? The volume change is certainly associated with the vibrations, i.e. the Einstein θ.

2. Can we handle of the invar effect? Combine volume with magnetic model?