Methods for storage of Gibbs energy data of substances

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ABSTRACT

There are two popular methods for storing Gibbs energy data for pure substances. They are inspired by Planck and by Lewis and Randall and may appear as very different but it will be demonstrated that they only differ by the choice of references. The derivation of functions to be stored will then be described and a crude but very simple method for extending them to 0 K by interpolation instead of extrapolation will be presented.

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1. Introduction

Chemical thermodynamics is primarily concerned with internal reactions in systems under constant pressure, temperature and content of matter. They can proceed spontaneously under decrease of the Gibbs energy and approach equilibrium at a minimum of Gibbs energy. Information has been obtained by studying transformations and reactions and results about equilibria have been collected and compiled, e.g. as equilibrium constants for reactions. One may express this kind of information as the change of Gibbs energy of a system when transforming from one well-defined state to another.

Due to the huge number of interesting reactions and transformations, it will be practically impossible to store all such information. In addition, such a compilation of information would contain an unlimited number of inconsistencies because each pure substance will take part in many reactions and experimental information is never exact. It would be more practical to use the information for evaluating and storing the thermodynamic properties of each substance separately. That is made by optimization of the fit to all information concerning a substance. Inconsistencies may then be minimized. The present report will not be concerned with the effect of pressure and a constant pressure of 1 bar will be assumed. Only problems connected to temperature will be discussed and P as a variable will thus be omitted from symbols in the following.

However, one cannot measure or study absolute values of the Gibbs energy of a pure substance, $°G_m^\varphi(T)$, only changes of Gibbs energy or differences. This problem is solved by instead studying and only storing values of the Gibbs energy of formation of the substance from a mixture of the component elements in well-defined states. In some connections one finds it convenient to compare with the component elements at the same temperature and one then compares with the most stable state of each element as a standard state, *STD*. One thus defines the standard Gibbs energy of formation,

$$\Delta_f °G_m^\varphi(T) \equiv °G_m^\varphi(T) - \Sigma x_i^\varphi °G_i^{STD}(T) \tag{1}$$

Lewis and Randall [1] suggested that the numerical value of the thermodynamic properties of a substance should be stored as $\Delta_f °G_m^\varphi(T)$.

It will be more complicated when one is concerned with variable temperature, e.g. when entropy or enthalpy is involved because they are obtained from the temperature derivative of the Gibbs energy. It will then be necessary to compare those with properties of the component elements at some fixed temperature and the choice has usually been 25 °C. In order to reserve the symbol $°G_i^{STD}$ for the standard states at the actual temperature, the new states will simply be regarded as some states of reference. To use $°G_i^{REF}(298.15 \text{ K})$ as reference for a Gibbs energy quantity is not possible because it would only represent a temperature independent quantity which would have the character of enthalpy. It should thus be replaced by $°H_i^{REF}(298.15 \text{ K}) - T°S_i^{REF}(298.15 \text{ K})$. However, Planck [2,3] proposed that one should use the entropies of the elements at 0 K instead of 298.15 K in order to take advantage of Nernst's heat theorem [4], also called the third law of thermodynamics, according to which the entropy at 0 K is the same for all allotropic modifications of an element as long as they are completely ordered. Planck further suggested that one should

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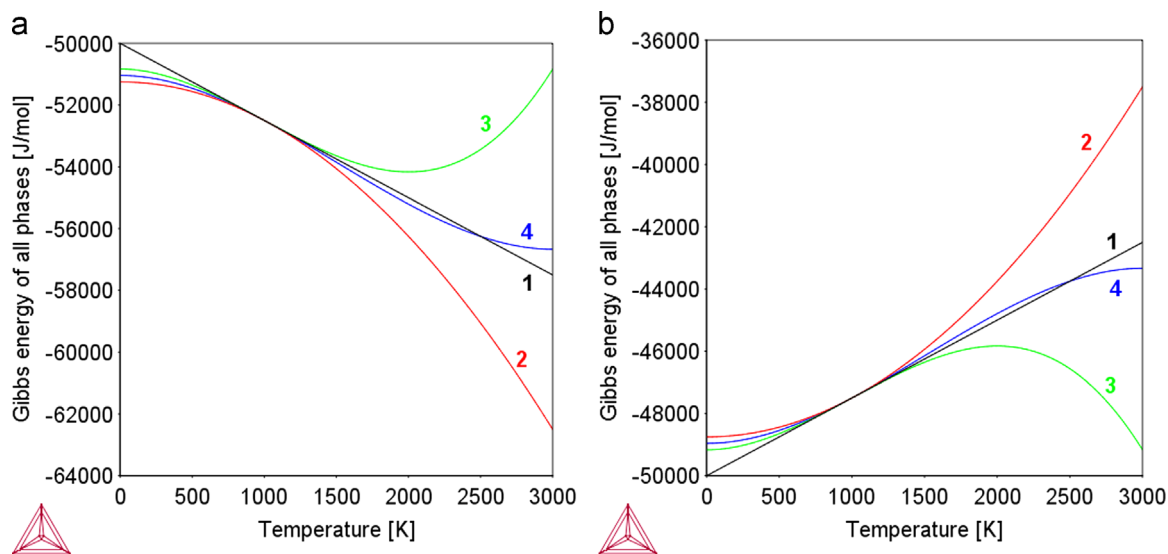
Fig. 1. Gibbs energy for the four different models and with (a) positive and (b) negative b-term. Curves 1: $a - bT$. Curves 2–4: $a - b(T + T_1(1 - T/T_1)^n/n)$ with Curves 2: $n=2$, Curves 3: $n=3$ and Curves 4: n is a combination of 2 and 3.

standardize this entropy value as zero for all the elements and also $\Sigma x_i^{\varphi} {}^{\circ}S_i$ (0 K) would then be zero for all compounds in well-ordered states. He further suggested that entropies expressed with this reference could be regarded as absolute entropies.

Planck's proposal and suggestion were applied to compilations of thermodynamic data by Lewis and Gibson [5] and were accepted for the JANAF Tables of thermodynamic properties [6] and more recently by SGTE (Scientific Group Thermodata Europe) [7] when an assessment of the thermodynamic properties of the elements was initiated in the late 1980s. SGTE recommended that the enthalpy reference for a pure element should be the enthalpy at 298.15 K for its most stable allotrope at that temperature and the symbol should be H_i^{SER}. For entropy the reference should be the value at 0 K evaluated for the stable allotrope for each element. In agreement with Planck's proposal, this value was set to zero but for clarity it will here be retained and be denoted ${}^{\circ}S_i^{\alpha}$ (0 K) and α will be the notation for all stable allotropes. For this allotrope one should thus evaluate and store the function

$$f_i^{\alpha}(T) = {}^{\circ}G_i^{\alpha}(T) - H_i^{SER} + T\,{}^{\circ}S_i^{\alpha}(0\,K) \tag{2}$$

This may be called the HSER method because the entropy reference is set to zero and thus omitted.

The SGTE assessment of the elements resulted in a unary database for the stable and several metastable allotropes of 78 elements published and compiled by Dinsdale in 1991 [8]. He could use previous assessments of the entropy difference between 298.15 and 0 K of the stable allotropes and so far his result was a HSER database. However, for the metastable allotropes there was hardly any information with a bearing on the entropy at low temperature. The information was usually limited to a high temperature range and concerned the difference in Gibbs energy from the stable allotropes. It was expressed through the so-called lattice stability introduced by Kaufman [9]. The information rarely permits more than a linear expression to be evaluated:

$$a - bT = {}^{\circ}G_i^{\beta}(T) - {}^{\circ}G_i^{\alpha}(T) \tag{3}$$

This implies that the metastable allotrope, β, has the same heat capacity as the stable one, α. The entropy of the stable α allotrope at 0 K is taken as the reference for entropy of each element and from Eq. (3) it is evident that the entropy at 0 K of the metastable β allotrope differs by b. It may be noted that this is in disagreement

with Nernst's heat theorem.

In a thermodynamic database the properties of all substances will be given relative to the references of the stable allotrope and in the present case they are thus given with the following function for a metastable allotrope of element i obtained by inserting ${}^{\circ}G_i^{\beta}$ from Eq. (3):

$$\begin{aligned} f_i^{\beta}(T) &\equiv {}^{\circ}G_i^{\beta}(T) - H_i^{SER} + T\,{}^{\circ}S_i^{\alpha}(0\,K) \\ &= {}^{\circ}G_i^{\alpha}(T) + a - bT - H_i^{SER} + T\,{}^{\circ}S_i^{\alpha}(0\,K) \end{aligned} \tag{4}$$

This is certainly a reasonable way of storing the properties of a metastable allotrope, considering the limited information, but the entropy part of $f_i^{\beta}(T)$ does not go to zero at 0 K if it does not for ${}^{\circ}G_i^{\beta}$.

The situation is often similar for stoichiometric compounds when the low temperature information is limited. It is thus common to express the standard Gibbs energy of formation with $a - bT$. By inserting this on the left hand side of Eq. (1) and applying the equation to a single element one obtains Eq. (3) because the most stable allotrope, α, is usually chosen as the standard state for the current temperature, STD. By generalizing Eq. (4) to include compounds one obtains

$$\begin{aligned} f_i^{\varphi}(T) &\equiv {}^{\circ}G_m^{\varphi}(T) - \Sigma x_i^{\varphi} H_i^{SER} + T\Sigma x_i^{\varphi}\,{}^{\circ}S_i^{\alpha}(0\,K) \\ &= \Sigma x_i^{\varphi}\,{}^{\circ}G_i^{\varphi}(T) + a - bT - \Sigma x_i^{\varphi} H_i^{SER} + T\Sigma x_i^{\varphi}\,{}^{\circ}S_i^{\alpha}(0\,K) \end{aligned} \tag{5}$$

To indicate that Eq. (5) also applies to compounds, the superscript α has been changed to φ. The heat capacity of the compound will here be equal to that for the average of the component elements. For that reason, the method has sometimes been applied with reference to the Neumann–Kopp rule which is actually based on the Gibbs energy of formation.

The justification for using Planck's method is the advantage of being able to replace uncertain extrapolations to low temperature with interpolation using the entropy at 0 K as a reliable piece of information once the properties of the stable allotropes of the component elements have been established by more reliable extrapolations. However, to exploit this possibility it is necessary to modify the $a - bT$ expression and force its entropy part, which now is b at all temperatures, to approach the value of the stable allotrope at 0 K. A method to achieve this will now be presented.