The Art and Science of Thermochemical Data Assessment

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Profound knowledge of experimental techniques and a large circle of friends around the world made Dr. O. Kubaschewski a leader in data assessment for high-temperature thermochemistry. He was a master of the use of data in graphical form, which served him better than highly-sophisticated programs. Considerable insight into the level of accuracy in the original studies gave Dr. Kubaschewski an unusual ability to foresee and evaluate the data without compromising the measured values. He understood how to use thermodynamic rules to optimize experimental data. New data are constantly being accumulated and the values recommended by Dr. Kubaschewski require changes, but his approach will always be invaluable.

Introduction

The field of inorganic thermochemistry provides abundant examples of chemical species that have been the major subject of research during the past 100 years [1897Ber]. Apart from their academic interest, these substances have been of interest in the many industrial applications that are made of inorganic materials from room temperatures to −3000 °C, and in all states of matter, solid, liquid, and gaseous [29Bic].

A particular scientific concern of the thermochemical properties is the many ways in which they are interrelated by simple equations, such as

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

where each of these quantities is accessible to independent measurement. It follows that this simple mathematical relationship provides a powerful tool for the assessment of the accuracy, consistency, and hence reliability of these three properties. The fact that these state functions are path independent also provides another consistency test, since the route of synthesis of a particular compound should have no effect on the overall change of these thermodynamic quantities, a relationship that is exemplified in the Hess law. It also follows that property values which are arrived at by the combination of data from a number of reactions contain the errors of each segment of the path embedded within their own error limits. Ultimately, the reliability of thermochemical data for compounds depends on the data for the chemical elements, but by convention, only the entropy content at 298.15 K is subject to uncertainty in this instance.

Our ability to measure any of these quantities with an acceptable accuracy has depended, of course, on the development of experimental techniques and equipment. The notorious difficulty of achieving successful measurements in the high temperature regime has had the result that measurements of the same quantity in the same temperature range by the same technique have not always produced satisfactory agreement among workers in different laboratories.

An attempt to correlate, interpret, and evaluate data on this vast material field needs a great deal of information and a skilful and peripatetic ability to acquire information and recommend acceptable values. Dr. O. Kubaschewski was the leading exponent in this field over the last half century by virtue of his deep knowledge of experimental procedures and data and also through his wide circle of friends and admirers around the globe [43Wei, 56Kub, 62Kub, 79Kub].

Kuba’s methods were not based on mathematical analysis in its most developed form but relied on two other aspects of scientific progress. The first of these was the reasonable appearance of the measurements in graphical form, which he interpreted with considerable insight. This insight included the conformity of the results to the general trend of behavior of similar materials and the degree of scatter of the results, when expressed in standard form, in comparison with the generally accepted experimental error limits of the technique. He also gave a weight factor to the origin of the measurements, whether the authors had previously published acceptable results using the given method, or were associated with a “school” renowned for its critical ability. His encyclopedic knowledge of the field, together with his intimate knowledge of the traditional development of the schools and their participants, gave him a unique overview. It will be observed that there was a great deal of human subjectivity in his mastery of the subject, but we hope to show during this discussion that some measure of subjectivity is laudable and, in fact, unavoidable in the task of data assessment.
Analysis of Compounds

The treatment of experimental data according to well-established statistical methods has become a relatively simple task in the last decade. This is because of the availability of desktop computers, and the relevant software for statistical analysis is now practically universal. There are, nevertheless, some precautions that must be observed even in the use of these convenient tools. Statistics, in their normally applied aspects, deal with random errors around a well-established analytical relationship between individual variables. The necessary condition for randomness in experimental data relates the number of results within a certain number of standard deviations, \( \sigma \), of the mean e.g. 95\% of the measurements within \( 2\sigma \) of the mean. Usually there are not enough values at any given level of the variables to apply this criterion, and the criterion is applied to the deviations from an assumed functional relationship. Thus the \( 2\sigma \) criterion in the case of a simple linear relationship is usually applied to the whole set of values of the variables rather than to any single values. As seen from a perusal of the literature for, say, heat capacity data, a number of functional relationships can be equally contemplated, and the best fit may apply only to one set of data. The relationship most commonly used, which was developed by K.K. Kelley [32Mai, 37Kel],

\[
C_p = \alpha + \beta T + \gamma T^2 + \delta T^2 \ldots \text{ etc.}
\]

has no physical basis, and so the termination of the “best fit” will usually be chosen at the point that the experimentalist or evaluator decides is adequate. The junction point chosen by the evaluator need not, then, coincide with the junction point of the mathematical “best fit.”

With the advent of powerful graphics software, it is highly recommended that the final equation be drawn out in full on the computer monitor so that it can be seen if the curvature that exists in the “best fit” seems to be reasonable also between the values of the variable where measurements have been carried out. It is frequently a chastening experience to extrapolate best fits for the heat capacity data of two crystallographic forms of the same substance to the transition temperature. The mathematical requirement here is that there should be continuity in the values of the Gibbs energy, the only discontinuities being in the heat content and entropy.

Within a given phase and crystal structure, it frequently happens that two temperature ranges can be fitted according to different polynomials of the type given above, but the resulting two equations must extrapolate to the same value and the same temperature differential at the point where the two representations meet. The proper mathematical approach would be to use a spline, which also requires that the second differential, or curvature, with respect to temperature should be continuous through the point of joining of the two equations. When one takes into account the experimental errors associated with measurement in the high-temperature field, it is normally forgivable when this harsher criterion is omitted.

The representation of second-order transformation is a particularly difficult matter using the Kelley expansion because of the lambda shape of the heat capacity/temperature curve around the transition temperature. The Kuba method for avoiding this difficulty was to treat the transformation as a first-order transition, which considerably simplifies the tabulation of data and only affects the calculated values for temperatures immediately around the transition temperature. Thus, whereas Barin and Knacke [73Bar] report the representation of the heat capacity of nickel around the Curie point by three equations:

\[
C_p(500 \text{ to } 631 \text{ K}) = -60.03 + 85.191 \times 10^{-3} T
+ 62.011 \times 10^{-5} \frac{T^2}{J/K \cdot \text{mol}}
\]

\[
C_p(631 \text{ to } 640 \text{ K}) = 111.662 - 162.72 \times 10^{-3} T \frac{J/K \cdot \text{mol}}{J/K \cdot \text{mol}}
\]

\[
C_p(640 \text{ to } 700 \text{ K}) = -92.184 + 96.612 \times 10^{-3} T - 156.437 \times 10^{-5} \frac{T^2}{J/K \cdot \text{mol}}
\]

Kuba [79Kub] suggests:

\[
T_{\text{transition}} = 631 \text{ K}
\]

\[
\Delta H_{\text{transition}} = 0.59 \text{ kJ/mol}
\]

which is very much simpler and equally as good above 700 K.

The treatment of heat capacity data at low temperatures for the elements almost completely determines the values that are arrived at for the entropies of the elements at 298 K. A survey of the literature, for example for copper, shows that nearly 100 different temperature-dependent equations have been proposed between 0 and 30 K, most of which use only the odd powers of temperature in the expansion [68Fur]. This plethora of information can be usefully summarized only by using all of the data to establish a standard deviation for the recommended entropy value in conjunction with the simplest temperature dependence that is consistent with the set. This is commonly known as “eyeballing the data,” a skill at which Kuba was a master. Such a procedure may offend the sensitivities of some experimentalists, but will serve the average user to within well-founded expectations. Time is a valuable sorting function for experimental data as Kuba showed when he tabulated the results for the heat of formation of Al2O3 over the last 100 years where the almost asymptotic approach to a generally accepted modern value is probably typical of experimental results [79Kub].

Entropy values for elements, such as Li and Na, which undergo a low-temperature martensitic transformation, are particularly susceptible to error [60Mar]. This is because it is almost impossible to reach equilibrium and establish accurately the degree of transformation at low temperature. In the absence of reliable transformation data for these elements, an unusually large error limit in the tabulated data for the \( S_{298} \) is not only prudent, but cannot be challenged at the present time.

Kuba’s “plus/minus” influence can clearly be discerned in the Richardson-Jeffes [48Ric] adaptation of the Ellingham diagram for the Gibbs energy of formation of metallic oxides. The error limits for these data were expressed by these authors by category letters A, B, C, and D representing a range from the most accurate values \( \pm 1000 \text{ cal/mole \text{O}_2(A)} \)