The applicability of least squares in the extraction of thermodynamic data from experimentally bracketed mineral equilibria

ROGER POWELL

Department of Geology, University of Melbourne, Parkville, Victoria 3052, Australia

TIM HOLLAND

Department of Earth Sciences, University of Cambridge, Cambridge, U.K.

ABSTRACT

The applicability of least squares in the extraction of thermodynamic data from experimentally bracketed mineral equilibria is considered primarily as a statistical (and logical) problem concerning the nature of the experimental data and the nature of the information to be extracted. The former relates particularly to the bracketed nature of the data, the latter to the requirement that not only thermodynamic data, but also the uncertainties in and the correlations between the data, are to be extracted. By examining the probability distributions, one can see that the majority of experimental brackets are approximately Gaussian distributed, primarily because experimental brackets are not generally very wide compared with experimental uncertainties on the bracket ends. Thus, using least squares on all the experimental brackets would be apposite for the thermodynamic data extraction problem. However, rather than fitting all the experimental brackets, we fit composite data formed from the individual experimental brackets for each experimentally determined reaction. It is shown that the use of composite data is equivalent to using all the brackets as long as the composite data are determined appropriately. The main reason for wishing to use composite data is that it allows the deleterious effect on the least squares caused by inconsistent brackets to be minimized. The uncertainties in very few of the composite data are large compared with the uncertainties in the ends of individual brackets. Therefore, least squares on composite data is appropriate for data extraction. Moreover, much of the uncertainty in the extracted thermodynamic data comes from uncertainty in the position of the bracket ends rather than the width of the brackets themselves.

INTRODUCTION

With the ever-increasing volume of experimental and calorimetric data on minerals, a thermodynamic data set, including data for most end-members of rock-forming minerals, is becoming attainable. An important stage in this development was the recognition that well-determined phase equilibria for reactions among mineral end-members provide excellent constraints on thermodynamic properties. So-called internally consistent data sets involve thermodynamic data calculated from such experimental data. Two methodologies have been used to do this, both involving processing all the experimental data (in some chosen system) at once. One is a mathematical programming (MAP) approach (Berman, 1988); the other is a least-squares (LSQ) approach (Powell and Holland, 1985; Holland and Powell, 1985, 1990—DS1, DS2, and DS4, respectively, DS standing for data sets). There have been some suggestions that various aspects of the LSQ approach make it inappropriate for data extraction: the aim of this paper is to show why the LSQ approach is not only sound, but also the most appropriate approach.

The essence of the application of LSQ to data extraction as followed in DS1–4 is now outlined. It will be assumed that entropy, volume, and heat-capacity data for end-members of minerals are relatively well known; therefore, the aim of data extraction is to calculate enthalpies of formation of end-members at 1 bar and 298 K (denoted ΔH_f) from the experimentally bracketed equilibria. The extension of the logic to cover the case where entropies and other parameters, in addition to enthalpies, are determined is considered in the discussion section below.

We will start by showing how reversal brackets for an experimentally determined reaction may be converted into an enthalpy of reaction representing all the reversal brackets for the reaction. Such enthalpy of reaction data are the input in our LSQ analysis. A typical set of reversal brackets for a reaction are shown in Figure 1a. If only enthalpies are to be found, the slope of the reaction is fixed; the two light dashed lines represent the limits of the range for the reaction if the ends of the brackets are taken to have no uncertainty. (For this example the reaction is taken to be one without curvature.) For each bracket in temperature, an equivalent bracket for the en-
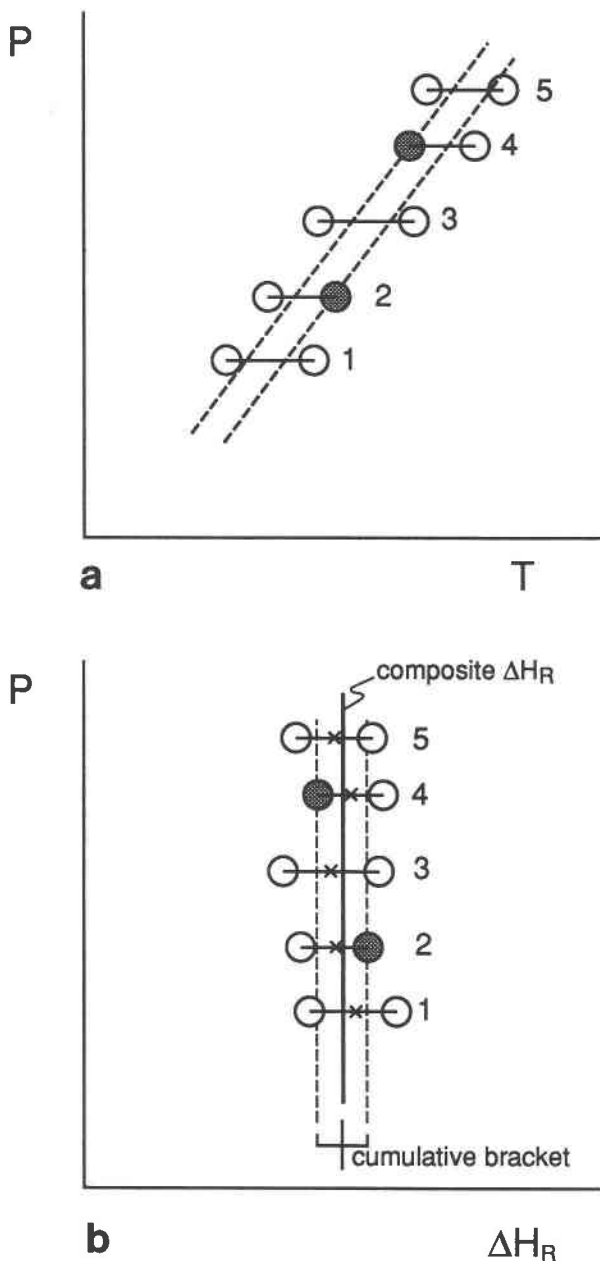
Fig. 1. The conversion of experimentally determined temperature brackets (**a**) into ΔH_R brackets (**b**), and the definition of cumulative brackets and composite ΔH_R (see text). (The shaded circles correspond to ΔH_R^{low} and ΔH_R^{high}.)

thalpy change of reaction, ΔH_R, can be calculated, Figure 1b (DS1, p. 332). Clearly the two bracket ends (shaded circles), which define the range of position of the reaction, also define the limits of ΔH_R if the ends of the brackets are taken to have no uncertainty. The resulting ΔH_R bracket shown at the bottom of Figure 1b is the cumulative bracket (of DS1–4), representing all the T brackets in Figure 1a. Alternatively, a composite ΔH_R may be defined in terms of, for example, a weighted average of the

midpoints of the ΔH_R brackets, marked by crosses, giving the solid vertical line in Figure 1b. Regardless of how the information in the individual ΔH_R brackets is combined, a representative ΔH_R value is generated, as well as some estimate of the uncertainty of this value.

Given a ΔH_R value and its uncertainty for each reaction in a set of reactions, the problem is to estimate the enthalpies of formation of the mineral end-members involved in the reactions. If there are the same number of reactions as enthalpies of formation being determined, then enthalpies of formation can be found for any specified position in each ΔH_R bracket. However there are normally more reactions than enthalpies of formation, so the problem becomes one of finding a consistent set of enthalpies of formation that agree with, or fit, the ΔH_R values in some sense. If the probability distribution representing each ΔH_R bracket is approximately Gaussian, then the way to find a best fit is by LSQ, in which the enthalpies of formation are found for which the sum of the squares of the departures of the calculated ΔH_R from the center of the ΔH_R bracket probability distribution, weighted to a measure of the width of the distribution, is minimized.

However, this development raises three questions: (1) The first, and the one that has been the main criticism of the LSQ methodology, is that the centers of the ΔH_R brackets are to be fitted, and therefore there will be a tendency to force reactions central to their brackets. This is contrary to the idea that a reaction should be placed anywhere within its bracket, and therefore it has been argued that LSQ is inappropriate. (2) It has also been suggested that even though LSQ and MAP give similar results, the uncertainties on the thermodynamic data as calculated by LSQ are meaningless. (3) It might also be argued that although an LSQ approach based on every experimentally determined bracket might be appropriate, in parallel to the MAP approach, which uses all brackets, the use of composite ΔH_R data is inappropriate. Discussion of these and related points is the focus of this paper. It will be shown that all of these concerns are unwarranted. We start with a consideration of the probability distribution of ΔH_R brackets corresponding to individual P-T brackets.

PROBABILITY DISTRIBUTION OF ΔH_R BRACKETS

In LSQ, the probability distribution of each datum to be fitted needs to be Gaussian for the method to be of maximum likelihood and for various optimal properties to apply. In fact, even if the distributions are unknown, LSQ is still optimal in a certain looser sense as the best linear unbiased estimator, e.g., Mood et al. (1974, p. 498–502). For LSQ to be appropriate in the more stringent case (Gaussian) for thermodynamic data extraction, the probability distribution of ΔH_R needs to be approximately Gaussian. We therefore start by deriving the probability distribution of ΔH_R brackets corresponding to individual P-T brackets. This probability distribution is directly related to the experimental uncertainty of the po-
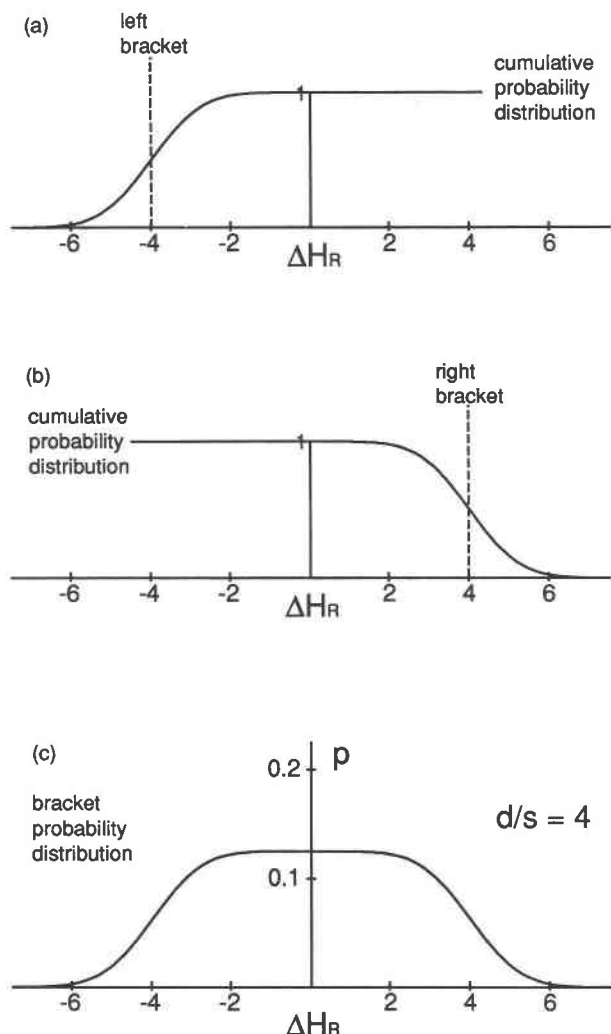
Fig. 2. The conversion of probability information for two limiting half-brackets into a bracket probability distribution. Part c is produced by multiplying the distributions shown in a and b and normalizing the result so that the area under the curve is 1.

Fig. 3. Bracket probability distributions calculated for d/s = −1, 0, 1, 2, 3, and 4.

sition of the ends of the half-brackets that define the bracket, or, in other words, the probability distribution of the ends of the half-brackets. Following the logic of Demarest and Haselton (1981), we take the probability distribution of the positions of the ends of the ΔH_R bracket to be Gaussian, with the mean and standard deviation of the distribution being found by simple error propagation from the uncertainties of the corresponding experimental brackets. The generation of the probability distribution of a ΔH_R bracket is illustrated in Figure 2 for a bracket centered on $\Delta H_R = 0$, with half-brackets at −4 and +4, and with unit standard deviations in the positions of the half-brackets. For the left bracket, the probability of the reaction being located at a particular ΔH_R is given by the area under the Gaussian distribution, centered on the position of the left bracket, from minus infinity to ΔH_R (Fig. 2a). For the right bracket, the proba-
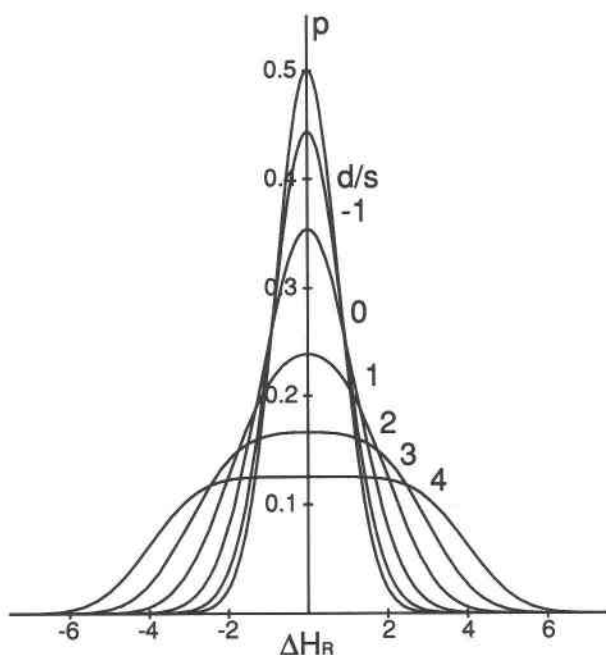
bility of the reaction being located at a particular ΔH_R is given by the area under the Gaussian distribution, centered on the position of the right bracket, from ΔH_R to plus infinity, Figure 2b. The combined probability from the contribution of both half-brackets, the so-called bracket probability distribution, is the product of the two distributions, normalized so that the area under the curve is 1 (Fig. 2c).

The shape of a bracket probability distribution depends on the relative magnitude of the bracket width and the uncertainty of the position of each half-bracket. Demarest and Haselton (1981), following Bird and Anderson (1973), describe this in terms of the parameter, d/s, in which d is half the bracket width, and s is the uncertainty (i.e., standard deviation) on the position of the end of each bracket. In Figure 2, the d/s is 4. As d/s is decreased, the flat top of the probability distribution gets narrower, until it is not noticeably flat for $d/s < 3$ (Fig. 3). As the application of LSQ relies on the data being Gaussian distributed, it is necessary to see how well these bracket probability distributions are approximated by Gaussian distributions. First, though, it is apposite to inquire what are the d/s values for the individual experimental brackets from which the composite data used in DS4 were calculated. Figure 4 shows that the majority of the experimental brackets have $d/s \leq 3$, with only 11% having more than this. In Figure 5, the bracket probability distribution for a range of d/s and equivalent Gaussian distributions are compared (the equivalent distributions were calculated so as to have the same probability at the center of the bracket). For $d/s \leq 2$, the distributions are essentially indistinguishable; even for $d/s \leq 3$, the agreement is good. The
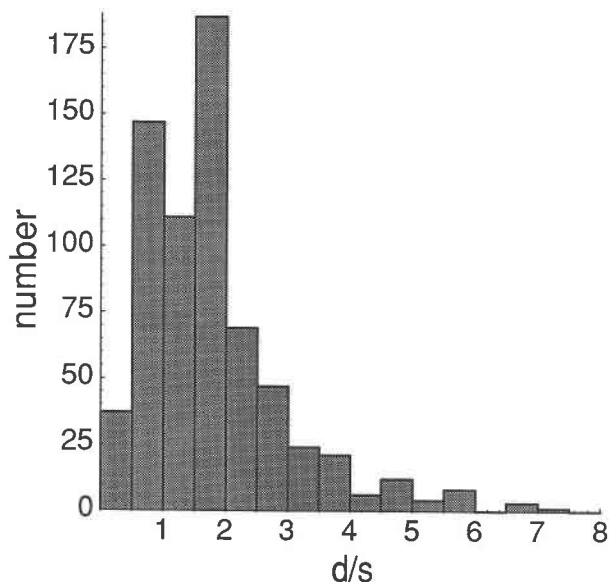
Fig. 4. A histogram of d/s values for all the individual ΔH_R brackets for the equilibria used in DS4.

Fig. 5. A comparison of bracket probability distributions and approximating Gaussian distributions for d/s = 1, 2, 3, and 4, with the Gaussian distribution formulated so that the approximating Gaussian has the same peak as the bracket probability distribution.

similarity between the bracket probability distributions and Gaussian distributions for most of the data means that concerns about the centralizing effect of using LSQ are unwarranted, even if all the individual brackets are used.

We determine values for the standard deviation of the reaction enthalpy $\sigma_{\Delta H_R}$ by matching an approximating Gaussian to the bracket probability distribution so that it has the same peak at the center of the bracket defined by d/s (Fig. 5). A least-squares fit yields $\sigma_{\Delta H_R}$ in terms of d and s as approximately:

$$\frac{\sigma_{\Delta H_R}}{s} = 0.887 + (d/s)(0.194 + 0.0973 d/s)$$

$$\text{for } d/s > -1 \qquad (1)$$

$$\frac{\sigma_{\Delta H_R}}{s} = 0.790 \qquad \text{for } d/s \leq -1.$$

We use these equations to calculate $\sigma_{\Delta H_R}$ from d/s for the individual brackets. Next we discuss whether the individual ΔH_R brackets or composite data should be used.

WHETHER TO USE COMPOSITE ΔH_R DATA?

There are two sides to the question whether composite ΔH_R data should be used. The first concerns the statistical validity of using composite data; the second concerns the advantages that accrue through using composite data. The main problem, which can be largely circumvented by using composite data, is the deleterious effect on LSQ of the ΔH_R brackets, which are inconsistent with the body of the data [resulting in $d/s < 0$ for the cumulative bracket (Fig. 6)]. The analysis must be made statistically robust, such that the presence of outliers does not prevent the trend through the majority of the data being found. In-
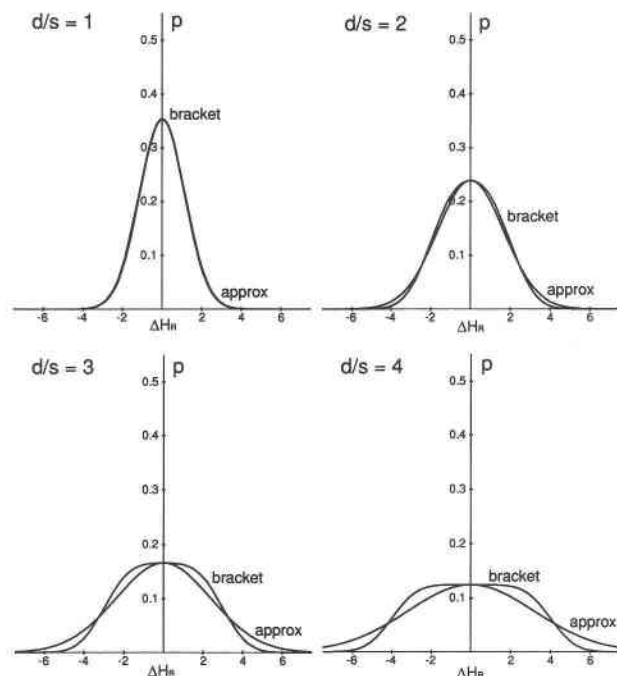
deed, such outlying brackets are a general problem—in the MAP analysis they are arbitrarily widened. Within the context of a set of brackets for an equilibrium, it is usually possible to identify half-brackets that are not consistent. In such a context, therefore, it is possible to determine a robust composite ΔH_R—one that is not sensitive to the position of any particular half-bracket in the set from which the composite value is determined. Additional advantages concern removing doubt about the distorting effect on the LSQ analysis of the 10% individual ΔH_R brackets, which are relatively wide (Fig. 4), given that very few of the cumulative brackets have d/s larger than 3 (Fig. 6). Also individual half-brackets can be incorporated in a natural way.

It remains to be shown that the use of composite data will give the same results as if all brackets were used. Consider the LSQ description, which is written in terms of all brackets (see also DS1): $\theta = (X^T V_y^{-1} X)^{-1} X^T V_y^{-1} y$. In this, θ is the vector of ΔH_f values being solved for, y is the vector of ΔH_R values being fitted, V_y is the covariance matrix of y [taken to be diagonal with diagonal elements $(\sigma_{\Delta H_R})^2$], and X is the coefficient matrix whose rows are just the reaction coefficients of the reactions corresponding to the ΔH_R values. With this written for every bracket, if, for example, the first experimental study involves n brackets, the first n rows of X will be identical, each being, say, x. However, the corresponding n values of y, $[y_1, y_2, \ldots, y_n]$, and their uncertainties in V_y, with diagonal el-

ements $[\sigma_1, \sigma_2, \ldots, \sigma_n]$, will vary, depending on the positions and widths of the brackets. With $\bar{y}$ as a central measure of the first n y values, then y_k may be written as $\bar{y} + \delta_k$, with δ_k being the difference from $\bar{y}$. If one denotes the part of X with the first n rows removed by X' and the corresponding part of y by y', then, after some algebra: $\theta = (X'^T V_y'^{-1} X' + rxx^T)^{-1}(X'^T V_y'^{-1} y' + r\bar{y}x^T + tx^T)$ with $r = \Sigma_{k=1}^n 1/\sigma_k^2$ and $t = \Sigma_{k=1}^n \delta_k/\sigma_k^2$. If the central measure used to calculate $\bar{y}$ is the weighted mean, then t is identically equal to zero, and $\theta = (X'^T V_y'^{-1} X' + rxx^T)^{-1}(X'^T V_y'^{-1} y' + rx^T\bar{y})$. Now, this can be reassembled into its original form, with the first n rows of X replaced by one row, x, and the first n elements of y replaced by one element, $\bar{y}$, if the corresponding element of V_y is $1/r$, i.e., with $\sigma = 1/\sqrt{r}$. Thus, in a LSQ problem with n identical rows in X, the n rows can be replaced by one row, if the problem is weighted properly, by means of V_y. This is the statistical justification for the use of composite data.

The remaining subject to consider is how composite data should be calculated, particularly so that they are robust with respect to outlying brackets.

CALCULATION OF COMPOSITE ΔH_R DATA

In the absence of outlying brackets, following directly from the logic in the last section, a composite ΔH_R value should be calculated as the weighted mean of the centers of the constituent ΔH_R brackets (Fig. 1b), with the uncertainty on this value being $1/\sqrt{r}$, calculated by (Eq. 1). One way of recognizing the presence of outlying brackets is to consider the d/s of the cumulative bracket, Figure 6. Clearly, if $\Delta H_R^{low} > \Delta H_R^{high}$ then d/s is less than zero, and the brackets are not consistent with each other. It is then necessary to identify the outlying brackets before calculating the composite ΔH_R value. As can be seen in Figure 6, this is a relatively common situation. We currently identify the outlying brackets using the median of the low ΔH_R brackets ends and the median of the high ΔH_R brackets ends. Further, the uncertainty on the composite ΔH_R value must be made larger, for example, by the exclusion of the terms from s corresponding to the outlying brackets. Although this approach is somewhat different from that employed in DS4, the results are essentially the same, not only in the values of ΔH_f of mineral end-members, but also in their uncertainties. The former is easy to understand, as there can be little argument about the choice of composite ΔH_R values. For the latter, any change in the algorithm for calculating uncertainties on composite ΔH_R values will tend to affect all the data in a similar way, so that uncertainties on ΔH_f will also be affected similarly. With the current weighting scheme, σ_{fit} is similar to that found in DS4 (about 1.6), and as σ_{fit} is the multiplier in the formula for the ΔH_f covariance matrix, the uncertainties are very similar. Such a value of σ_{fit} seems appropriate, given that there is some scatter in the experimental data being fitted, so that a value slightly larger than that predicted by χ^2 for consistency would be expected.
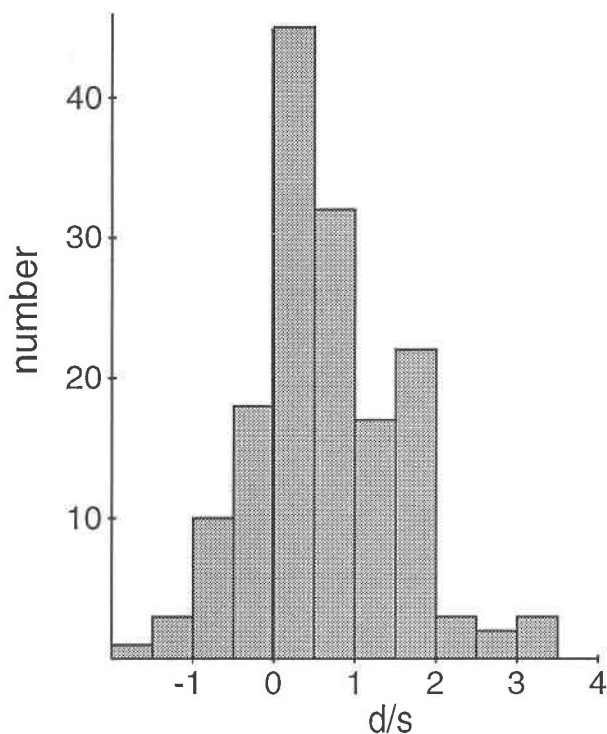

Fig. 6. A histogram of d/s values for the cumulative brackets of the equilibria used in DS4, excluding reactions in which only a particular end-member occurs (in which case the reaction would be fitted centrally regardless of the probability function used). The d/s values are calculated using $d/s = (\Delta H_R^{high} - \Delta H_R^{low})/(\sigma_{\Delta H_R^{low}} + \sigma_{\Delta H_R^{high}})$, in which ΔH_R^{low} is the highest low ΔH_R bracket end, $\sigma_{\Delta H_R^{low}}$ is its uncertainty, ΔH_R^{high} is the lowest high ΔH_R bracket end, and $\sigma_{\Delta H_R^{high}}$ is its uncertainty. The value $d/s < 0$ corresponds to $\Delta H_R^{low} > \Delta H_R^{high}$, and there is no consistent region.

DISCUSSION AND CONCLUSIONS

Having established that LSQ is an appropriate methodology for extracting thermodynamic data from experimentally bracketed equilibria, the power of LSQ in allowing the calculation of uncertainties in and correlations between the thermodynamic data can be reiterated. An important observation concerning these uncertainties comes from the distribution of d/s for the experimental equilibria (Fig. 4) and the shapes of the bracket distribution functions (Fig. 5). For $d/s \approx 1$, i.e., for much of the data, the major component of the distributions relates to the possibility of the equilibria being outside the brackets. As a consequence, the main contribution to the calculated uncertainties is likely to come from the uncertainties on the ends of the brackets, not the width of the brackets themselves. It is for this reason that Engi and Lieberman (1990), using Monte Carlo simulation in conjunction with MAP to estimate uncertainties on extracted thermodynamic data, reached the erroneous conclusion that uncertainties must be essentially nonexistent.

The formally correct way to proceed in the data extraction problem, treating the LSQ methodology as just

a special case of maximum likelihood with the data being Gaussian distributed, would be to derive a method of maximum likelihood using the bracket probability distribution. This is straightforward, but applying it would be tedious because there is no closed form for the solution. Moreover, as the greatest majority of the data are essentially Gaussian distributed and the few remaining equilibria with large σ_s are not critical to the analysis, little would be gained for the considerable amount of extra effort expended. If entropies, for example, in addition to enthalpies, are also to be constrained in the data extraction, the LSQ logic is still appropriate, if the overall analysis is considered to be iterative, with the focus on enthalpies of formation but with entropies changing between iterations.

We conclude with a quote from DS4: "Both LSQ and MAP are capable of providing reliable and similar analyses of the experimental data, each with its advantages and disadvantages. However, we believe that the ability of the least squares method to provide the uncertainties, and their mutual correlations, of the calculated thermodynamic data makes this [the LSQ method] the preferable method of analysis."

ACKNOWLEDGMENTS

REFERENCES CITED

Berman, R.G. (1988) Internally consistent thermodynamic data for minerals in the system $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$. Journal of Petrology, 29, 445–522.

Bird, G.W. and Anderson, G.M. (1973) The free energy of formation of magnesian cordierite and phlogopite. American Journal of Science, 273, 84–91.

Demarest, H.H., and Haselton, H.T., Jr. (1981) Error analysis for bracketed phase equilibrium data. Geochimica et Cosmochimica Acta, 45, 217–224.

Engi, M., and Lieberman, J. (1990) Thermodynamic data for rock-forming minerals: How close to the truth? Eos, 71, 1649.

Holland, T.J.B., and Powell, R. (1985) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations. II. Data and results. Journal of Metamorphic Petrology, 3, 343–370.

——— (1990) An internally consistent thermodynamic dataset with uncertainties and correlations: The system $Na_2O-K_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-C-H_2-O_2$. Journal of Metamorphic Petrology, 8, 89–124.

Mood, A.M., Graybill, F.A., and Boes, D.C. (1974) Introduction to the theory of statistics (3rd edition), 541 p. McGraw-Hill, New York.

Powell, R., and Holland, T.J.B. (1985) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations. I. Methods and a worked example. Journal of Metamorphic Petrology, 3, 327–342.