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An internally consistent thermodynamic dataset with uncertainties and correlations: 1. Methods and a worked example

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Abstract. This, the first two papers, sets out the philosophy and methods of determining an internally consistent thermodynamic dataset for minerals using the least squares method. The applicability of the least squares method is discussed, and it is applied to a small set of experimental equilibria in the system Na_2O–Al_2O_3–SiO_2–H_2O. The importance is stressed of defining not only the enthalpies of formation of minerals, but also the uncertainties and the correlations among them. The system which has been used as an illustration for this paper serves as a visual guide to the method, as it is small enough to represent graphically in two dimensions. In the paper which follows, we extend the method to a system of 60 equations (experimentally determined equilibria) involving 34 unknowns (enthalpies of formation of mineral end-members).

Key words: least squares method; thermodynamic dataset

INTRODUCTION

The proliferation of mineral analyses, made possible by the widespread use of the electron microprobe, has led to increasingly more detailed studies of the nature of equilibrium in metamorphic rocks. With this improvement in analytical facilities has come a wider awareness of the possibilities offered by the application of equilibrium thermodynamics to metamorphic rocks, with the often implicit assumption that these represent a frozen-in state of equilibrium, attained at some unspecified stage of the metamorphic evolution. Equilibrium thermodynamics generally can be applied successfully in two distinct ways. The first method involves the calculation of the deflection of experimentally determined P–T curves, due to solid solution of end-members other than those present in the experiments, in the minerals of interest. This is essentially the approach of conventional geothermometry and geobarometry. The second method involves creating a thermodynamic database from which any equilibrium reaction may be calculated, so long as the dataset encompasses reliable data for all phases in the desired reaction. It is this second approach which, to us, seems so attractive in principle and potentially so simple in practice. This approach has been applied successfully in the past (Powell, 1973, 1978; Helgeson, Delaney, Nesbitt & Bird, 1978) and is becoming increasingly useful in metamorphic petrology.

Thermodynamic calculations of the stability of mineral assemblages in rocks, assuming a frozen-in equilibrium among the minerals, can be performed if thermodynamic data for a group of useful mineral end-members are known, and activity-composition relations in the minerals are understood. The principal problem is the acquisition of a reliable set of enthalpies of formation of mineral end-members, because calorimetrically-determined enthalpies, although often well-determined, are not sufficiently precise for calculation purposes. The reason for this is that in the calculation of the enthalpy of reaction, a difference, often small, is taken between several large numbers. Another lesser problem is that entropies, although quite sufficiently precise through measurement, may require incremental addition to account for substitutional or positional disorder. In most cases it is the unknown, or only imperfectly known state of Al-Si disorder, in alumina-bearing silicates, which causes the problem. Estimation of the entropy increment over and above the third law calorimetric value, although bounded, is usually approximate at best.

A solution to these problems is to use high P–T, experimentally determined mineral equilibria

to constrain the thermodynamic data. The resulting dataset may be referred to as internally consistent if such an approach is followed. Earlier attempts include those of Powell (1978) and Helgeson *et al.* (1978) and although these differ in several important aspects, they both involve an essentially incremental approach, in that individual reactions or blocks of several reactions are used in sequence to derive the thermodynamic dataset. The main drawbacks of this incremental approach are:

(a) Values calculated early in the sequence of operations are taken as subsequently fixed; thus it is not clear whether the final dataset is optimal in any sense;

(b) It is difficult to ascertain uncertainties on, and correlations between, the derived enthalpies in the dataset. The principal source of these uncertainties lies in the uncertainties in the determination of the experimental equilibria used (eg., Powell, 1985).

The first point above is particularly relevant if there are calorimetrically measured constraints on enthalpies of formation. Injudicious decisions early in a sequence, may propagate through to yield calculated enthalpies which are not in good agreement with calorimetrically determined values. The second point above is critical; the major advantage of having an internally consistent dataset is lost, if uncertainties on enthalpies of reaction, and thus uncertainties on calculated temperatures and pressures, cannot be calculated.

A solution to the dataset problem, which satisfies these criteria, is to use a least squares approach to calculating enthalpies of formation. This paper presents this method, and includes a small but illustrative worked example on a subsystem of the major dataset. The next paper presents the results of applying the least squares approach to the whole system of 43 mineral end-members. The least squares approach allows the simultaneous generation of all the thermodynamic data, using all the selected reliable mineral equilibria. It also provides a covariance matrix for the dataset, thus enabling error propagation calculations to be performed when applying these data to rocks.

CALCULATION METHOD

The equilibrium relation for a balanced chemical reaction is (see Table 1 for notation):

$$0 = \Delta G^\circ + \mathrm{RT} \ln K.$$

For each of the end-member mineral phases, the free energy contribution to ΔG° is (e.g. Powell, 1978):

$$\Delta_f H(1,298) - TS(1,298) + \int_{298}^{T} Cp \, \mathrm{d}T - T \int_{298}^{T} \frac{Cp}{T} \mathrm{d}T + PV(1,298)\,(1+\alpha(T-298)-\beta P/2) \quad (1)$$

Note that we include thermal expansions and isobaric compressibilies. Although the effects of α and β are small, and tend to cancel in many reactions, they can be important in some solid–solid reactions, and certain devolatilization reactions at high pressures. (Note that β is multiplied by P^2 in (1)).

Table 1. Notation; thermodynamic properties are in units of kJ, K and kbar

$\Delta_f H$	enthalpy of formation from the elements at 1 bar and 298 K; in the context of the least squares analysis, **h** is a vector of these values.
S	entropy at 1 bar and 298 K
V	volume at 1 bar and 298 K
Cp	heat capacity: $Cp = a + bT + cT^{-2} + \mathrm{d}T^{-1/2}$, with T in K
α	coefficient of thermal expansion: usually grouped with V as αV
β	coefficient of isothermal compressibility: usually grouped with V as βV
ΔG°	Gibbs energy change for a reaction among pure end-member phases at the temperature and pressure of interest
K	equilibrium constant for a balanced reaction

ab	high albite	$NaAlSi_3O_8$
pa	paragonite	$NaAl_3Si_3O_{10}(OH)_2$
and	andalusite	Al_2SiO_5
ky	kyanite	Al_2SiO_5
jd	jadeite	$NaAlSi_2O_6$
cor	corundum	Al_2O_3
q	quartz	SiO_2
H_2O	H_2O fluid	H_2O

For the fluid species end-members H_2O and CO_2, the corresponding expression is:

$$\Delta_f H(1,298) - TS(1,298) + \int_{298}^{T} Cp \, \mathrm{d}T - T \int_{298}^{T} \frac{Cp}{T} \mathrm{d}T + \mathrm{RT} \ln f \quad (2)$$

The fugacity term above is expressed as a simple low order polynomial, such that at each pressure RT ln f has a quadratic form (Holland, 1981):

$$\mathrm{RT} \ln f = a + bT + cT^2$$

In this expression, a, b and c are functions of pressure determined by a new fit to the fugacity of H_2O data of Burnham, Holloway & Davis (1968), including the extrapolation to high pressure of Delancy & Helgeson (1978), and a new fit to the CO_2 data of Shmonov & Shmulovich (1974) and also including the

higher pressure extrapolations of Bottinga & Richet (1981).

The coefficients of the expressions are given in Table 2, and represent the H_2O data in the range 1–30 kbar and the CO_2 data in the range 1–15 kbar. The fit to the fugacity data for H_2O data is better than 0.3 kJ at 1 kbar, and better than 0.2 kJ at higher pressures, with an overall residual standard deviation of 0.105 kJ. For CO_2 the data fit is better than 0.2 kJ, with a standard deviation of residuals of 0.12 kJ. Figure 1 shows the function RT ln f as a function of T for a range of pressures.

THERMODYNAMIC DATA

A dataset for petrological purposes requires certain information: inspection of (1) and (2) shows that the data required are heat capacities, molar volumes, entropies, thermal expansions, compressibilities and enthalpies of formation. It is our experience (and that of Helgeson *et al.*, 1978) that all of the above data are readily available, or can be reliably estimated, with the exception of enthalpies of formation of minerals. If we can accept a set of all the former quantities, our problem is reduced

Table 2. RT ln f for H_2O and CO_2 are expressed as $a + bT + cT^2$. (a) The expressions for a, b and c in terms of P (in kbar) are given; (b) then the values of a, b and c; (c) then the values of a, b and c for a series of pressures. The factor at the head of the c column implies that the column entries are to be multiplied by 10^{-6}.

(a) $a = a_1 + a_2P + a_3P^2$
$b = b_1 + b_2P^{-1} + b_3P^{-2} + b_4P^{-1/2}$
$c = c_1 + c_2P + c_3P^{-2} + c_4P^{-1/2}$

(b)

	H_2O	CO_2
a_1	−38.61	−9.429
a_2	1.3854	2.6209
a_3	-1.228×10^{-3}	−0.011704
b_1	0.12716	0.12772
b_2	0.03977	0.11587
b_3	-7.8802×10^{-3}	−0.02725
b_4	−0.041436	−0.14323
c_1	-9.8194×10^{-6}	-6.806×10^{-7}
c_2	6.5419×10^{-8}	-2.3744×10^{-7}
c_3	1.3849×10^{-6}	0.0
c_4	-1.390×10^{-5}	-5.677×10^{-6}

(c)

	H_2O			CO_2		
P	a	b	c $\times 10^{-6}$	a	b	c $\times 10^{-6}$
1	−36.88	0.11762	−25.04	− 6.82	0.07311	−6.59
2	−35.49	0.11578	−19.86	− 4.24	0.07756	−5.17
4	−32.74	0.11590	−16.59	0.87	0.08337	−4.47
6	−29.99	0.11666	−15.14	5.87	0.08780	−4.42
8	−27 26	0.11736	−14.23	10.79	0.09114	−4.59
10	−24.53	0.11796	−13.58	15.61	0.09374	−4.85
12	−21.81	0.11846	−13.06	20.34	0.09584	−5.17
14	−19.11	0.11889	−12.63	24.97	0.9758	−5.52
16	−16.41	0.11926	−12.25			
18	−13.72	0.11958	−11.92			
20	−11.04	0.11987	−11.62			
22	−8.38	0.12012	−11.35			
24	−5.72	0.12035	−11.09			
26	−3.07	0.12055	−10.85			
28	−0.43	0.12074	−10.62			
30	2.20	0.12091	−10.40			

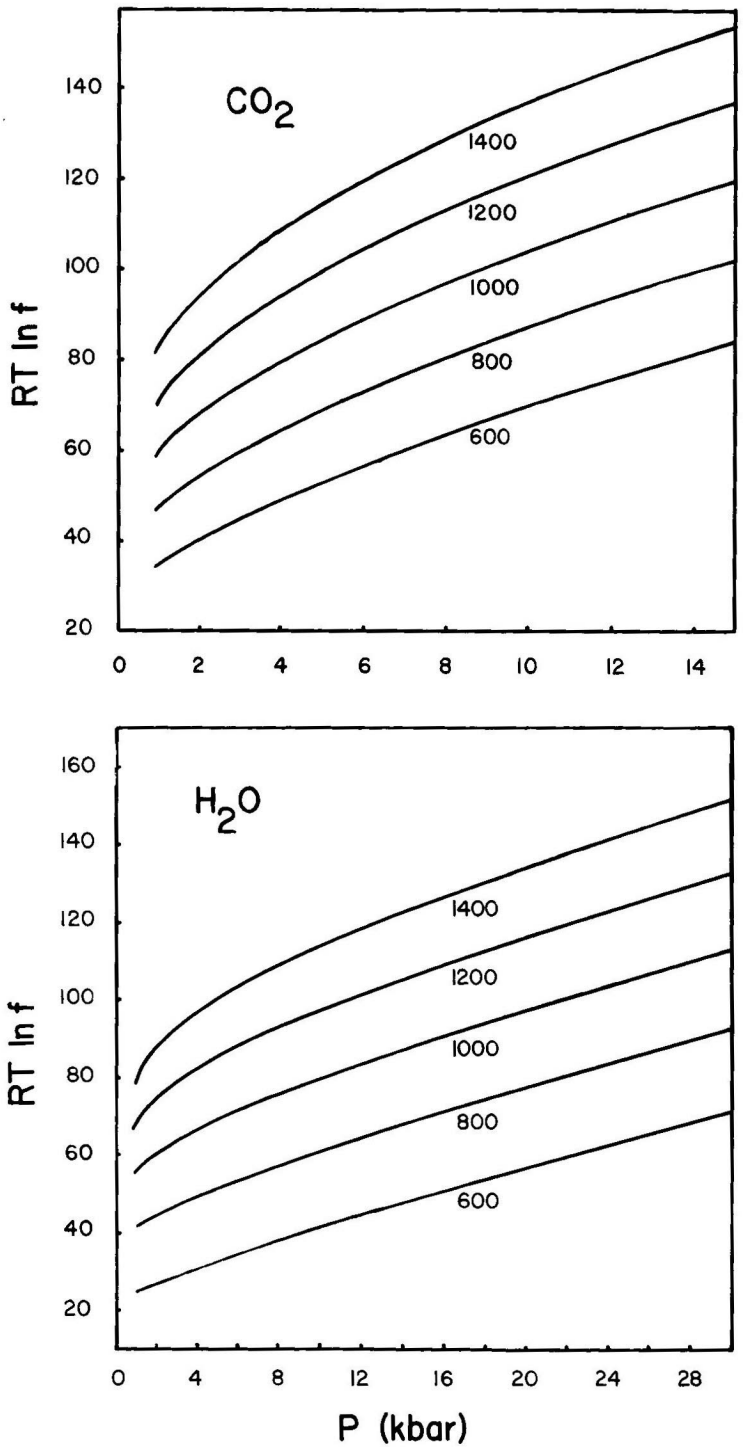

Fig. 1. RT ln f plots for CO_2 and H_2O, calculated from the polynomials given in Table 2. Temperature contours are given in Kelvins.

to that of determining enthalpies from the available P–T experimental phase equilibrium studies. For our purposes we accept the methodology and data fitting described by Holland (1981) as far as heat capacities, volumes and entropies are concerned. The sources for all the data used are given in the second paper; however, we wish to describe our methods of representing thermal expansion and compressibility data for minerals, and of estimating these parameters when measured data are lacking. This is followed by a discussion of entropies and cation disorder.

Thermal expansion

Measured volume data at 1 bar are fitted by a linear equation for the temperature range 298–1100 K:

$$V(1,T) \simeq V(1,298) + a(T-298)$$

where a, from (1), can be seen to be $\alpha V(1,298)$. Where data are lacking, we note that the value of α is approximately constant for minerals with the same structure (e.g. 3.2 for sheet silicates, 3.0 for chain silicates, 2.4 for garnets, etc), allowing reasonable estimates for unknown mineral end-members.

Isothermal compressibility

In similar fashion, measured molar volume data at 298 K are fitted by a linear equation for the pressure range 0–30 kbar:

$$V(P,298) \simeq V(1,298) - bP$$

where b, from (1), can be seen to be $\beta V(1,298)$. For mineral end-members where volume data at high pressures are lacking, we employ an approach modified from Wang (1978), which is based on elastic constant systematics for isostructural compounds. Wang noted a correlation of compressibility with volume to the fourth power for compounds with constant mean atomic weight. For silicates we have plotted log β against log (mean atomic volume) and show straight line contours for mean atomic weight in Fig. 2. The slope for mean atomic weight contours is -4, as suggested by Wang. Undetermined compressibilities were estimated by interpolation and extrapolation of the known data using this plot.

Entropies and cation disorder

Third law entropies are determined by integrating Cp/T with respect to T from as near $T=0$ K as is experimentally feasible, up to $T=298$ K.

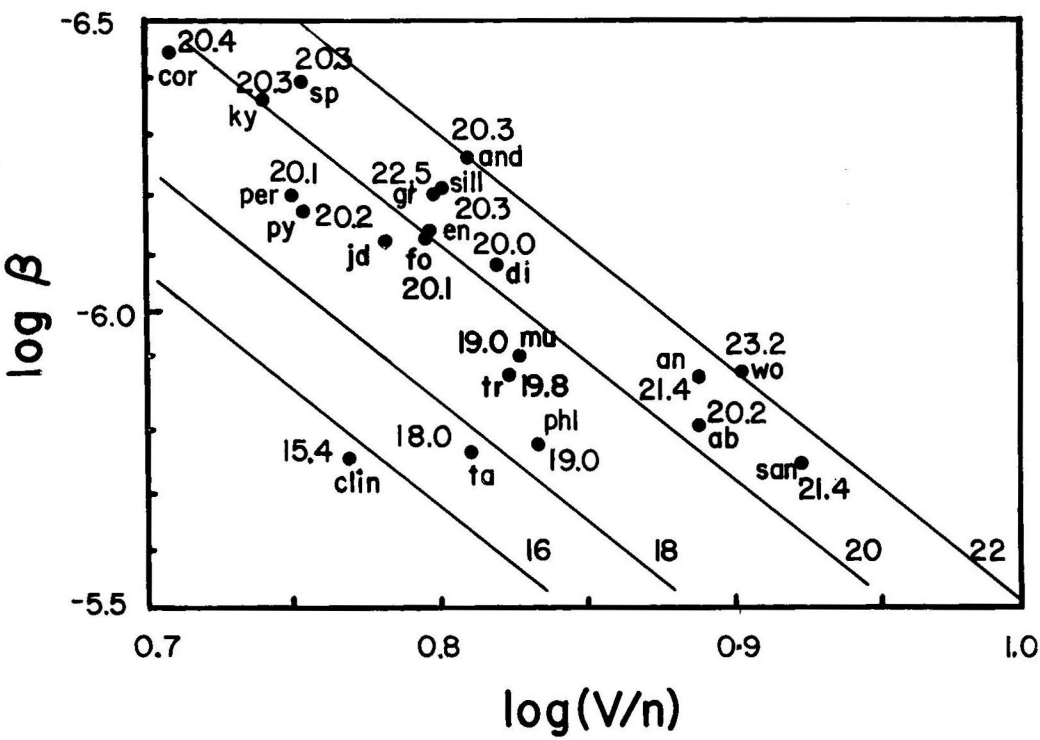

Fig. 2. Compressibility systematics, in terms of log β against log (V/n), contoured for molecular weight divided by n, the number of atoms in the formula. Curves drawn with slope of -4 following the suggestion of Wang (1978).

Such calorimetric determinations, in general, yield minimum estimates of entropy, because any disorder in a mineral is usually frozen-in, and does not contribute to the specific heat at these low temperatures. As an example, high albite has a substantial (but not complete) degree of Al-Si disorder, which contributes to its entropy, a contribution not determinable from calorimetry. It is a well-known phenomenon that such a mineral will order at low temperatures, if kinetics allow, and, in general, will attain moderate to high degrees of short-range order even if long-range order is kinetically impeded (Putnis & Bish, 1983; Fyfe, Klinowski, Putnis & Thomas, 1983). X-ray determinations of Al-Si ordering invariably indicate considerably less order than actually exists because of the averaging effect of sampling a very large number of unit cells. Modern studies on Al-Si ordering in cordierite, indicate very high degrees of short-range order even when X-ray methods would suggest complete disorder (Carpenter, Putnis, Navrotsky & McConnell, 1983). We, therefore, prefer to *minimize* any entropy increment for phases (even high albite) which show disorder. In the case of albite, the equilibrium experiments on the breakdown to jadeite+quartz indicate much less than maximal disordering entropy (Holland, 1980). This is in contrast to the assertions of Hemingway, Krupka & Robie (1981), who prefer to envisage totally disordered analbite. It will be our practice to operate with entropies which reflect the ordered state, unless the phase equilibrium data require incrementing the entropy of a particular phase, and then only a minimal increment will be applied to satisfy the experimental dP/dT slopes.

ACTIVITIES OF CO_2 AND H_2O IN FLUID MIXTURES

A number of equilibria, used here, involve mixed H_2O–CO_2 fluids. The mixing properties of CO_2–H_2O are at present not well known. The modified Redlich-Kwong (MRK) equation of state probably provides as reasonable a model as any, and has the distinct advantage of prediction over a geologically useful range of pressures and temperatures. However, the number of adjustable parameters needed in this empirical approach is not clear, and as yet there is no exact test of the success of the various adaptions of the MRK equation. The version of Kerrick & Jacobs (1981) provides reasonable agreement between experimental and calculated equilibria in T-x_{CO_2} space, as demonstrated by Jacobs & Kerrick (1981). Although this is not a sensitive test, we use their version of the MRK equation as a starting point in this work. Bearing in mind the unknown errors in the model activities generated by the MRK equation, and the added disadvantage computationally, we have opted for a compromise; we have taken the activity data of Kerrick & Jacobs (1981) and have made a fit to their results using a pressure and temperature dependent subregular (asymmetric) solution model. The derived values of $w(CO_2)$ and $w(H_2O)$, as linear functions of pressure and temperature, are:

$$w(H_2O) = 8.3 - 0.007T + 0.26P$$
$$w(CO_2) = 17.8 - 0.014T + 0.38P$$

in kJ mole^{-1}, with T in K and P in kbar. The resulting activities at a number of temperatures and pressures are shown in Fig. 3. These parameters were derived for the range 2–10 kbar and 400–800°C. At $P \leq 1.5$ kbar we use $w(CO_2) = 25 - 0.025T$ (kJ) and $w(H_2O) = 1.08 - 0.012T$ (kJ), with T in K. Until better measured data become available, we do not feel that anything more sophisticated is justifiable.

GEOMETRY OF THE PROBLEM

Given that the enthalpy of reaction is assumed to be the only unknown for each experimentally determined reaction, the enthalpy of reaction for the P–T curve to pass through the end of a reversed bracket, can be calculated as:

$$\Delta H = T\Delta S - P(\Delta V + \Delta(\alpha V)(T-298) - \Delta(\beta V)P/2) - \int_{298}^{T} \Delta Cp \, dT + T \int_{298}^{T} \frac{\Delta Cp}{T} \, dT - \Sigma \, r_i \, RT \ln f_i - RT \ln K$$

where P and T are the conditions at the end of the experimental bracket, K is the equilibrium constant calculated from the compositions of the phases in the experiment, and the r_i, are the reaction coefficients of the fluid species, H_2O and CO_2. The experimentally determined P–T reversals bracket the enthalpy of reaction, brackets on the high T side giving an upper bound on the enthalpy of reaction, brackets on the low T side giving a lower bound.

The situation is complicated by the fact that there are experimental uncertainties on the positions of the reversal brackets themselves. These uncertainties are frequently not reported, or are only cursorily alluded to in the literature. To simplify the calculations, we assume that all experimental runs are characterized by the following uncertainties: temperature ±5°C, pressure ±0.2 kbar at higher pressures (piston-cylinder runs) and

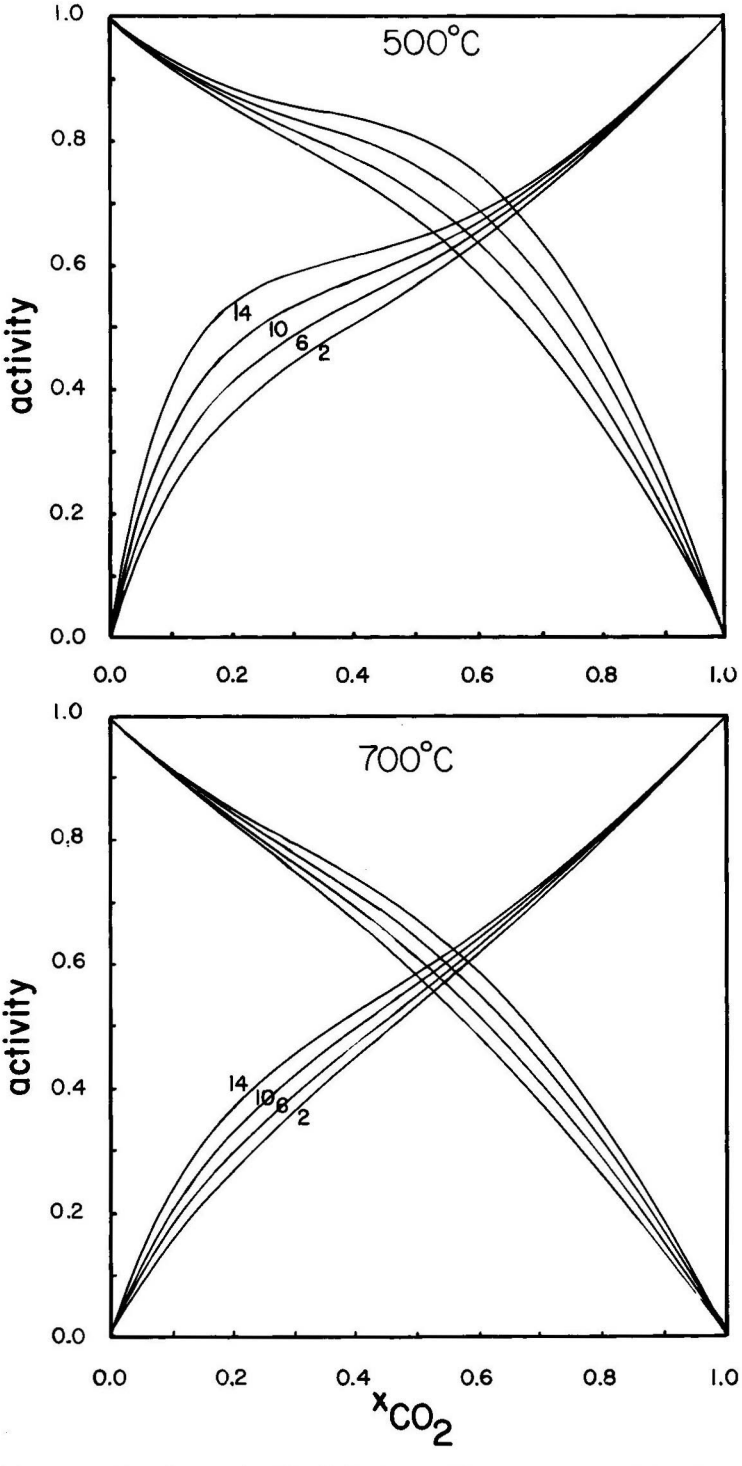

Fig. 3. Activity–composition diagrams for CO_2–H_2O mixtures. These were generated from the subregular parameters given in the text.

± 0.02P kbar at lower pressures (gas apparatus and hydrothermal rod bombs). The least squares results are not sensitive to these assumptions.

The system NASH (Na_2O–Al_2O_3–SiO_2–H_2O) will be used as an illustration of our method and approach to the dataset problem. In this system, experimental data for five reactions, Table 3, are used to determine the enthalpies of formation of high albite and paragonite. Enthalpy data for the other phases (quartz, jadeite, corundum, H_2O and kyanite, andalusite) are assumed known for the purpose of this example. Of these, the enthalpies of the first four must be assumed, to anchor the thermodynamic properties, by tying in to *jd* as a reference for Na_2O, *cor* for Al_2O_3, *q* for SiO_2, and H_2O for H_2O. The enthalpies of *ky* and *and* are also taken as known so that the geometry of this system is kept simple for ease of graphical portrayal.

Table 3. The reactions in NASH for which experimental equilibrium data are available

(1) $jd + q = ab$
(2) $pa = jd + ky + H_2O$
(3) $pa = ab + cor + H_2O$
(4) $pa + q = ab + and + H_2O$
(5) $pa + q = ab + ky + H_2O$

For this system, enthalpy of reaction brackets, from the data in Table 4, are shown in Fig. 4. The enthalpy of reaction, which corresponds to each experimental bracket, is represented in Fig. 4 by a box. This should strictly be represented by a trapezoid inscribed within the box to account for correlation of uncertainties between ΔH and T. Figure 4a shows, for example, that the series of experimental brackets defines a consistent range for the enthalpy of reaction. An algorithm is required to convert this distribution of enthalpy brackets into a single bracket on ΔH which represents the experimental data for the particular reaction. It is necessary to define a lower bound on this bracket width to prevent an unrealistically narrow bracket, in the event that the individual error boxes overlap (as in Fig. 4c). We adopt the notation of Demarest & Haselton (1981), but use it for the accumulated data for a reaction, using d for the half-width of the consistent range in ΔH of reaction, and s for the uncertainty at each end of the bracket that corresponds to experimental uncertainties. A suitable lower bound on bracket width is $d/s = 1$, so that the bracket on ΔH cannot be smaller than twice the uncertainty introduced by experimental uncertainties. Such an enthalpy bracket corresponds closely to that suggested by Demarest & Haselton (1981) for $d/s \ll 2$. The enthalpy brackets, calculated in this way are given in Table 4, and shown by bold lines in Fig. 4. It is important to realize that although we would prefer the eventual calculated enthalpy of reaction to lie within this bracket, there is a finite probability that it will not.

Using the enthalpy of reaction brackets shown in Fig. 4, the thermodynamics of the five reactions involve two unknowns, the enthalpies of *ab* and *pa*. Using the data in Table 5, the enthalpy brackets may be transformed into coordinates of $\Delta_f H(ab)$ and $\Delta_f H(pa)$ and are illustrated in Fig. 5. The shaded area is the consistent region for acceptable solutions to the enthalpies of formation of *ab* and *pa*. Again there is a finite probability of the actual values lying outside this region, and of course there is a possibility that no region of consistency exists. Such a situation might arise if there are problems in the experimental equilibrium data or in some of the thermodynamic parameters assumed known.

METHODS

Although the acceptable region can be readily defined as above (and illustrated in Fig. 5), we require a representation of this region which yields an optimal solution and information about the spread (or standard deviation) of values which the enthalpies of *ab* and *pa* can take, and, in addition, information about the correlation which may exist between these values. Without such a representation we cannot estimate (by standard error propagation techniques) the uncertainties in position of a P–T curve which has been calculated for any reaction involving these phases. Until now, no-one has attempted to do this.

Earlier attempts at defining comprehensive sets of internally consistent thermodynamic data (Powell, 1973, 1978; Helgeson *et al.*, 1978) were based on an incremental approach. This was defensible in the sense that the problem was simplified—the set in Powell (1978) was generated in a week using a pocket programmable calculator. However, both the experimental phase equilibrium dataset and the thermodynamic data (entropies, heat capacities, etc) sets have grown in size and quality in recent years, so that an approach, which tackles all reliable reactions to solve for all unknowns simultaneously, is now possible.

Table 4. Enthalpy of reaction systematics. P(kbar) and T(°C) refer to ends of experimentally determined brackets; H(low) and H(high) are the corresponding enthalpy of reaction values in kJ: calc is the calculated temperature or pressure using the least squares results; ± is the corresponding $\pm(2\sigma)$. The calculated enthalpy of reaction bracket derived from the experiments is given in the form (h_1<–>h_2), with h_1 and h_2 being the low and high limits respectively; calc(H) is the calculated enthalpy of reaction using the least squares results; uH is a measure of the enthalpy of reaction equivalent to the experimental uncertainty on a measured pressure and temperature; d/s is defined in the text.

Reaction and source	x(CO2)	P(kbar)	T(C)	H(low)	H(high)	calc	±	summary
jd + q = ab								
(Holland, 1980)	-	16.5 16.0	600	11.36	12.16	16.33	0.27	H : (11.22 <-> 12.30)
	-	22.0 21.0	800	11.13	12.70	21.67	0.28	calc(H) = 11.64 (sd 0.22)
	-	25.0 23.5	900	10.59	12.92	24.33	0.28	uH = 0.54, d/s = 0.7
	-	27.5 26.0	1000	10.80	13.10	26.95	0.28	
	-	30.0 29.0	1100	10.96	12.47	29.55	0.29	
	-	33.0 31.0	1200	10.31	13.29	32.11	0.29	
pa = jd + ky + H2O								
(Holland, 1979)	0	24.0 26.0	550	79.31	81.38	25.32	0.40	H : (80.29 <-> 81.25)
	0	24.0 25.5	600	79.82	81.36	24.84	0.40	calc(H) = 80.68 (sd 0.20)
	0	24.0 25.0	650	80.29	81.31	24.38	0.40	uH = 0.24, d/s = 2.0
	0	23.0 24.5	700	79.74	81.25	23.93	0.41	
pa = ab + cor + H2O								
(Chatterjee, 1970)	0	1.0	530 550	102.42	104.18	527	6	H : (101.61 <-> 102.69)
	0	2.0	555 575	101.86	103.49	558	6	calc(H) = 102.11 (sd 0.26)
	0	3.0	580 600	101.80	103.37	584	7	uH = 0.54, d/s = -0.6
	0	5.0	625 640	101.63	102.74	631	7	
	0	6.0	620 650	99.69	101.87	653	7	
	0	7.0	650 670	100.38	101.81	674	7	
pa + q = ab + and + H2O								
(Chatterjee, 1972)	0	1.0	470 490	95.63	97.32	480	6	H : (95.95 <-> 97.00)
	0	2.0	510 530	96.23	97.80	513	6	calc(H) = 96.49 (sd 0.25)
	0	3.0	540 560	96.31	97.81	542	7	uH = 0.52, d/s = 0.3
	0	4.0	560 580	95.70	97.16	571	7	
	0	5.0	590 600	95.91	96.62	598	7	
pa + q = ab + ky + H2O								
(Chatterjee, 1972)	0	5.0	570 625	90.57	94.01	598	7	H : (91.55 <-> 92.74)
	0	6.0	600 630	91.34	93.17	616	7	calc(H) = 92.32 (sd 0.22)
	0	7.0	620 640	91.55	92.74	633	8	uH = 0.43, d/s = 1.4

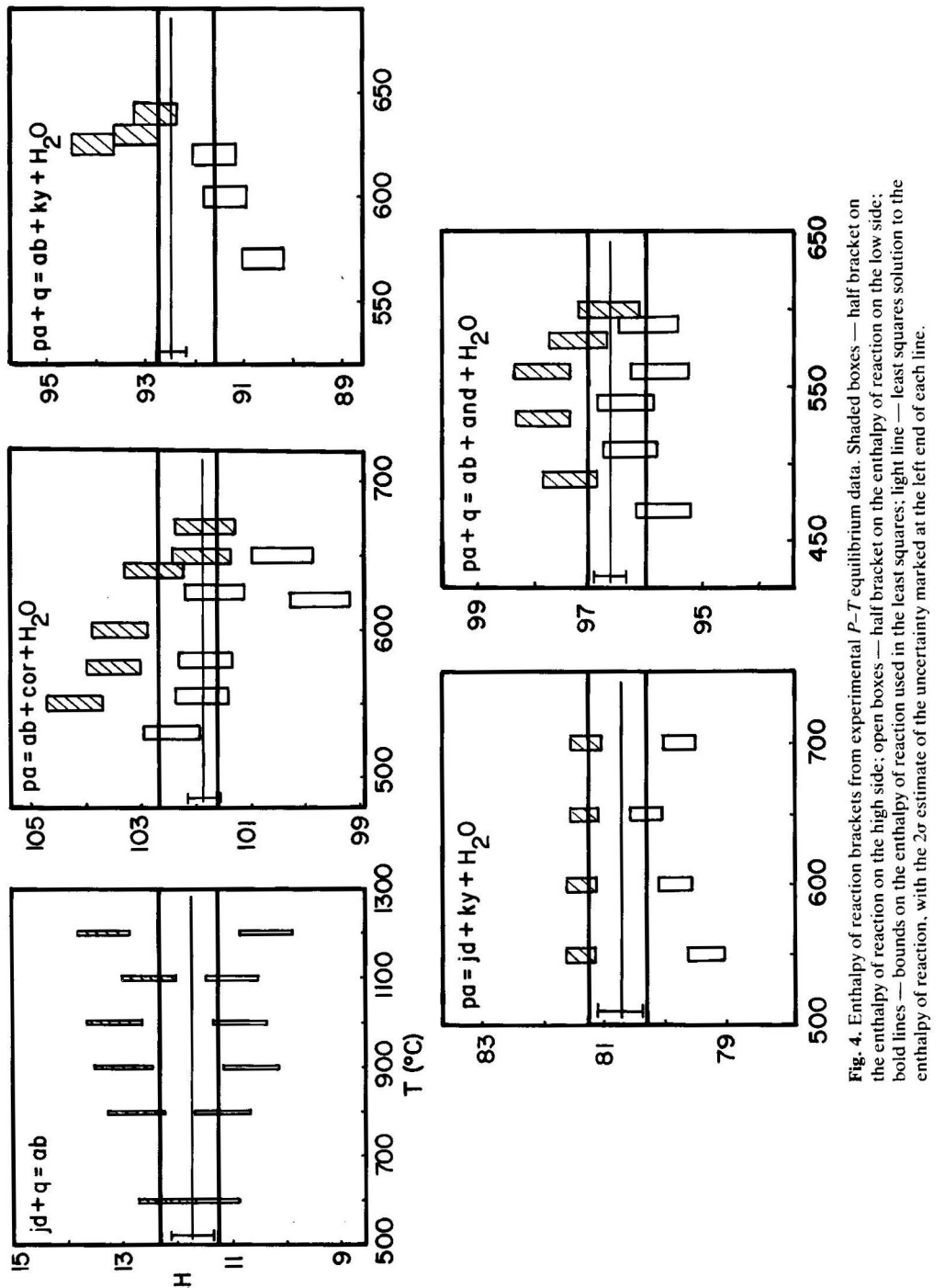

Fig. 4. Enthalpy of reaction brackets from experimental P–T equilibrium data. Shaded boxes — half bracket on the enthalpy of reaction on the high side; open boxes — half bracket on the enthalpy of reaction on the low side; bold lines — bounds on the enthalpy of reaction used in the least squares; light line — least squares solution to the enthalpy of reaction, with the 2σ estimate of the uncertainty marked at the left end of each line.

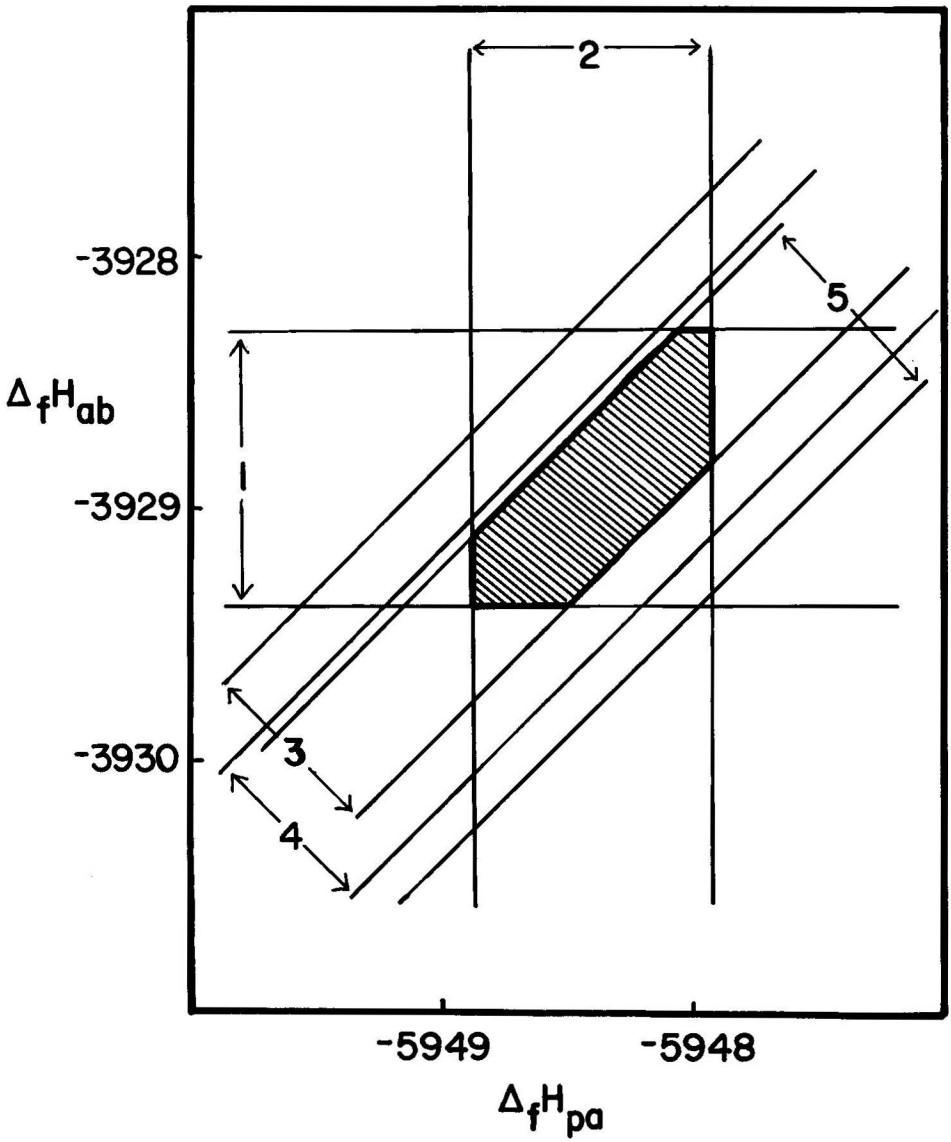

Fig. 5. Enthalpy brackets for the five reactions in NASH, and the consistent region in terms of $\Delta_f H_{ab}$ and $\Delta_f H_{pa}$.

Furthermore, the determination of uncertainties and correlations is now a viable proposition.

The main approach to this problem (in the literature) is one which involves using each side of an experimentally derived enthalpy bracket for a reaction as a linear inequality, and solving the set of inequalities using linear programming (e.g. Gordon, 1973; Halbach & Chatterjee, 1982). However, there are several problems with this method:

(1) It is assumed that the enthalpy for a reaction corresponds to a uniform distribution, the probability of the enthalpy of reaction lying outside the bracket being zero. This implies the absence of experimental errors such as imprecision or inaccuracy in P or T measurement.

(2) The linear programming method identifies a vertex of the consistent region (for example a corner of the shaded region in Fig. 5), corresponding to minimizing or maximizing some function. It does not naturally identify the 'centre' of the acceptable region.

(3) Linear programming methods provide no means of representing the shape of the consistent region.

The linear programming approach does have one very important advantage in that the non-existence of a consistent region is immediately recognized. This is particularly important in problems of a multi-dimensional nature where recognition might be difficult—problems which would be obvious in our simple two-dimensional example. In fact we have used, in our initial survey of the experimental data, a less elegant equivalent approach to perform this task.

An alternative approach is that of least squares minimization, an approach which has the considerable merit of providing estimates of uncertainties on the parameters solved for, as well as the parameters themselves. Of course, it must be demonstrated that the least squares approach is a sensible way of extracting the enthalpies of formation from experimental bracketing data. Demarest & Haselton (1981), in presenting a logical statistical analysis of the meaning of experimental brackets (and therefore enthalpy of reaction brackets), concluded that a least squares approach should not be in error if the ratio d/s (with d and s defined as above), for each bracket, was less than 1, with 2 being an upper limit. The reason for this is that if the bracket is too wide, the way least squares attempts to force a central value in the bracket interval will be misleading; however, an appropriate weighting scheme, using bracket width, is capable of minimizing this effect. Of course, the approach advocated here involves combining the P,T brackets into an enthalpy of reaction bracket before least squares is applied, so the logic of Demarest & Haselton is not directly applicable. However, by analogy, least squares is applicable here as long as a weighting scheme is incorporated to take account of the different d/s values of the enthalpy brackets for the different reactions. We conclude that weighted least squares, as advocated here is a valid approach to the internally consistent dataset problem.

We use matrices to set up the least squares problem. To introduce this, using **b** for the vector of enthalpies of reaction for a set of reactions, then:

$$\mathbf{b} = \mathbf{Rh} \text{ or } b_i = \Sigma R_{i\,j} h_j$$

where **R** is the matrix of reaction coefficients, and **h** is the vector of enthalpies of formation of the end-members involved in the reactions. In our example, there are five reactions and eight end-members. Given the vector of enthalpies of reaction, **b**, the centres of the enthalpy of reaction brackets calculated from the experimental data, we wish to calculate the vector of enthalpies of formation, **h**, in a least squares sense, by minimizing:

$$\|\mathbf{b}-\mathbf{Rh}\|^2.$$

In our example:

$$\mathbf{h}^T = \begin{matrix}\text{enthalpies of formation of}\\ [\ ab\ \ pa\ \ and\ \ ky\ \ jd\ \ cor\ \ q\ \ H_2O\ ]\end{matrix}$$

$$\mathbf{R} = \begin{bmatrix} 1 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\ 0 & -1 & 0 & 1 & 1 & 0 & 0 & 1 \\ 1 & -1 & 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & -1 & 1 & 0 & 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 1 & 0 & 0 & -1 & 1 \end{bmatrix}$$

$$\mathbf{b} = \begin{bmatrix} \Delta H(jd+q=ab) \\ \Delta H(pa=jd+ky+H_2O) \\ \Delta H(pa=ab+cor+H_2O) \\ \Delta H(pa+q=ab+and+H_2O) \\ \Delta H(pa+q=ab+ky+H_2O) \end{bmatrix}$$

This is solved in the conventional way (e.g. Belsley, Kuh & Welsch, 1980, p. 69–72) by:

$$\mathbf{h} = (\mathbf{R}^T\mathbf{R})^{-1}\mathbf{R}^T\mathbf{b}.$$

As it stands, this equation will not suffice because there are five reactions and eight unknowns. One aspect of this has been discussed earlier; that the enthalpies of formation must be anchored. The way to do this is to add rows to **R**, each one being of the form:

$$[0,0,\ \ldots\ .,0,1,0,\ \ldots\ .,0,0],$$

with the one in the position of the anchor, and the anchor value being added to the corresponding element of **b**. This can be viewed as adding synthetic 'reactions' to the system of equations. Calling the matrix of added rows to **R**, **S**, and the added values to **b**, **c**. For our example, the first two rows of **S** fix the enthalpies of formation on *ky* and *and*, the remaining rows are for the anchors:

$$\mathbf{S} = \begin{bmatrix} 0&0&1&0&0&0&0&0 \\ 0&0&0&1&0&0&0&0 \\ 0&0&0&0&1&0&0&0 \\ 0&0&0&0&0&1&0&0 \\ 0&0&0&0&0&0&1&0 \\ 0&0&0&0&0&0&0&1 \end{bmatrix} \quad \mathbf{c} = \begin{bmatrix} -2591.60 \\ -2595.70 \\ -3029.94 \\ -1675.70 \\ -910.70 \\ -241.81 \end{bmatrix}$$

The solution is then:

$$\mathbf{h} = (\mathbf{R}^T\mathbf{R}+\mathbf{S}^T\mathbf{S})^{-1}(\mathbf{R}^T\mathbf{b}+\mathbf{S}^T\mathbf{c}).$$

The remaining feature to incorporate is weighting. The weighting factor for the enthalpy bracket part is a diagonal matrix, $\mathbf{W}_1$, whose elements are equal to the reciprocal of some

proportion of the bracket width. We have used a quarter of the bracket width, taking the bracket as 2σ. Although more sophisticated weighting schemes can be envisaged, our experience is that the least squares results are not particularly dependent on the weighting scheme employed. $\mathbf{W}_1$ here is:

$$\mathbf{W}_1 = \begin{bmatrix} 1/0.27 & 0 & 0 & 0 & 0 \\ 0 & 1/0.24 & 0 & 0 & 0 \\ 0 & 0 & 1/0.27 & 0 & 0 \\ 0 & 0 & 0 & 1/0.26 & 0 \\ 0 & 0 & 0 & 0 & 1/0.30 \end{bmatrix}$$

The weighting for the anchor part is a diagonal matrix, $\mathbf{W}_2$, whose elements are equal to the reciprocal of the standard deviation of the mean of the calorimetric measurements. An anchor value with no uncertainty can be simulated by making the appropriate diagonal value of $\mathbf{W}_2$ large. $\mathbf{W}_2$ here is:

$$\mathbf{W}_2 = \begin{bmatrix} 1/0.83 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/0.83 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2.09 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/0.65 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/0.50 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/0.02 \end{bmatrix}$$

The justification for this weighting scheme is that it ensures that the residuals on **b** and **c** have equal variance (eg Belsley *et al.*, 1980, p. 195). The least squares solution now becomes:

$$\mathbf{h} = (\mathbf{R}^T\mathbf{W}_1^2\mathbf{R} - \mathbf{S}^T\mathbf{W}_2^2\mathbf{S})^{-1}\ (\mathbf{R}^T\mathbf{W}_1^2\mathbf{b} + \mathbf{S}^T\mathbf{W}_2^2\mathbf{c}) \quad (4)$$

The least squares logic provides an estimate of the uncertainties on the parameters, **h**, through the covariance matrix $\mathbf{V}_\mathbf{h}$:

$$\mathbf{V}_\mathbf{h} = (\mathbf{R}^T\mathbf{W}_1^2\mathbf{R} + \mathbf{S}^T\mathbf{W}_2^2\mathbf{S})^{-1}.$$

Initially, to complete the worked example, we use large values for all the diagonal elements of $\mathbf{W}_2$ (i.e. no uncertainties on calorimetric values), before using a realistic $\mathbf{W}_2$. This has the effect of reducing the problem to just two dimensions, involving $\Delta_f H(ab)$ and $\Delta_f H(pa)$ as unknowns, to correspond with Fig. 5. The result of substitution into (4) is:

$$\Delta_f H_{ab} = -3928.9 \text{ kJ}$$
$$\Delta_f H_{pa} = -5948.3 \text{ kJ},$$

with the remaining enthalpies of formation as specified. Also:

$$\mathbf{V}_\mathbf{h} = \begin{bmatrix} 0.040 & 0.027 \\ 0.027 & 0.038 \end{bmatrix},$$

with the remaining variances as specified, and the remaining covariances zero. From this:

$$\sigma_{\Delta_f H_{ab}} = \sqrt{0.040} = 0.20 \text{ kJ}$$
$$\sigma_{\Delta_f H_{pa}} = \sqrt{0.036} = 0.19 \text{ kJ}$$
$$\rho_{\Delta_f H_{ab}\,\Delta_f H_{pa}} = 0.027/(\sqrt{0.040}\ \sqrt{0.036}) = 0.72.$$

A graphical representation of this two-dimensional least squares problem is instructive, and is shown in Fig. 6. The central lines of the enthalpy brackets are shown together with the least squares solution derived from them. The covariance matrix ellipse, at the 2σ level, is also shown. Thus we see, in a graphical demonstration, the relationship between the acceptable region, based on bracketing of the equilibria, and the covariance ellipse. Although there must be a mismatch between an ellipse and a polygon, the ellipse provides a good representation, as long as it is accepted that the predicted probability of the solution being located in a corner of the consistent region is somewhat smaller than it should be. In multi-dimensional space, occupied by the larger system in the next paper, we must generalize our notions to imagining a multi-dimensional ellipsoid representing a polygonal consistent region.

Using a realistic $\mathbf{W}_2$ in (4) makes the problem eight-dimensional, so it can no longer be illustrated graphically. The first two columns of Table 5a show the resulting enthalpies of formation, and Table 5b shows the correlations between these enthalpies of formation. There are several things to note. A complicating factor concerns *ky* and *and*, the enthalpies of which are considered fixed here even though they are not anchors. A consequence of this is that their enthalpies are changed slightly, and the standard deviations on their enthalpies reduced, as a consequence of the regression. This does not happen with anchors; the important thing that does happen is that the experimental equilibria introduce correlations between the enthalpies of the anchors. In comparison with the least squares with large $\mathbf{W}_2$, the uncertainties on the enthalpies of formation of *ab* and *pa* are much larger, and the correlation between them is much stronger. This is a direct consequence of the propagation of the uncertainties in the anchor values through to the least squares results. However, it is important to realize that the resulting covariance matrix gives the *same* calculated uncertainties on the enthalpies of the reactions used in the least squares. This will not be true, in general, for other reactions, which are not linear combinations of those used.

ERROR PROPAGATION

The estimated parameters and covariance matrix can be used to calculate the temperature

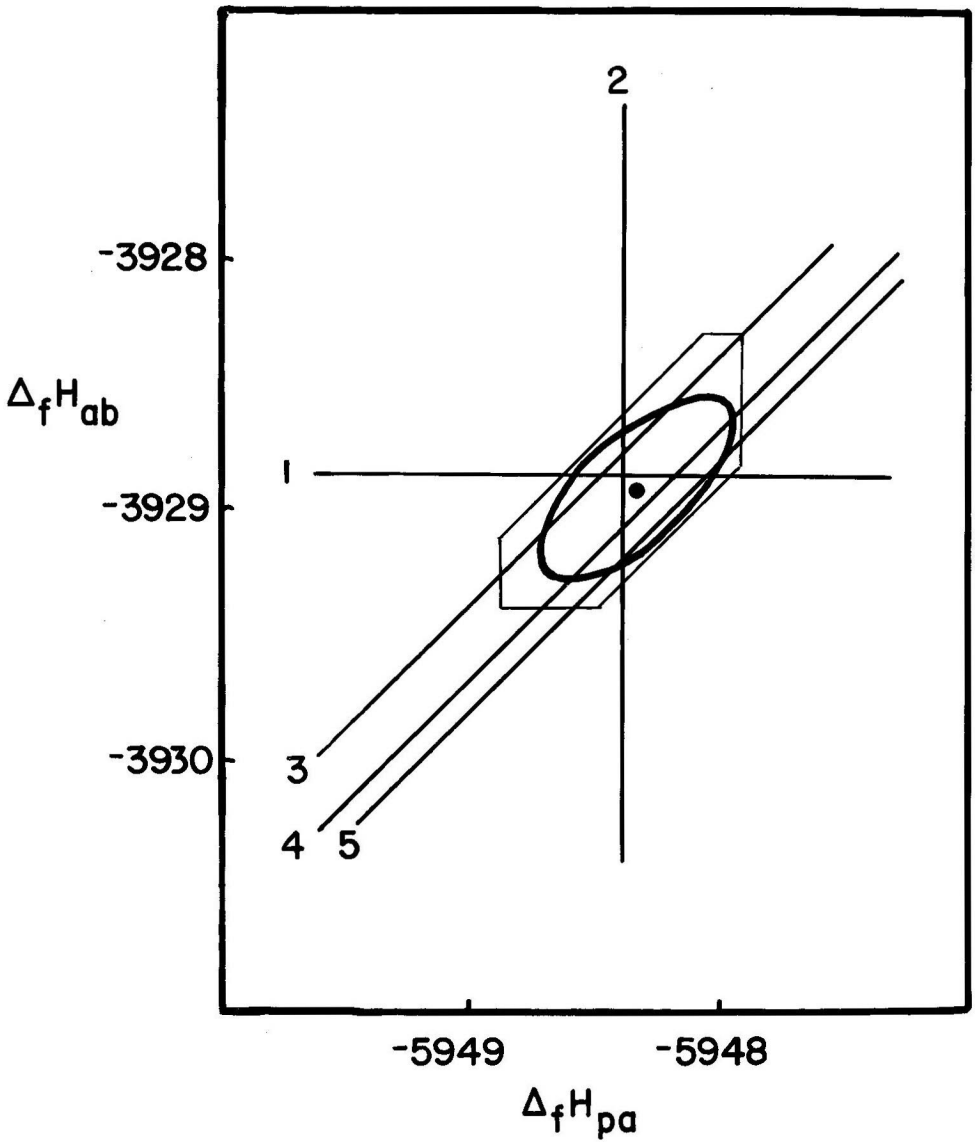

Fig. 6. The least squares solution and covariance matrix error ellipse in relation to the consistent region and the central lines of the enthalpy of reaction brackets.

on each of the original experimental brackets, as well as the estimated uncertainty on this temperature. Using standard error propagation techniques (e.g. Powell, 1985):

$$\sigma_T^2 = \left(\frac{\partial T}{\partial \mathbf{h}}\right)^T \mathbf{V_h} \left(\frac{\partial T}{\partial \mathbf{h}}\right).$$

We find the partial derivatives by finite difference. An analagous expression can be written for σ_P. Results using this equation are included in Table 4. The calculated uncertainties on temperatures and pressures are generally smaller than the original experimental brackets because of the constraining effect of considering all the reaction equilibria simultaneously.

The importance of considering the correlations between individual enthalpies of formation is made clear for the case of the reaction $jd + q = ab$; the uncertainty $\sigma_{\Delta H}$ on the enthalpy of reaction is given, for $\Delta H = H_{ab} - H_{jd} - H_q$, by $\sigma_{\Delta H}^2 = \mathbf{JVJ}^T$, where $\mathbf{J}$, the jacobian, is:

$$\left[\frac{\partial \Delta H}{\partial H_{ab}} \quad \frac{\partial \Delta H}{\partial H_{jd}} \quad \frac{\partial \Delta H}{\partial H_q}\right]$$

Table 5. (a) Thermodynamic properties (units: kJ, k, kbar) of end-members in the illustrative system. The first two columns are least squares results (see text). H, σ_H, S, V are molar enthalpy, sigma (enthalpy), entropy, and volume respectively; a, b, c, d refer to heat capacity polynomials where $c_p = a + bT + cT^{-2} + dT^{-1/2}$; αV and βV are products of molar thermal expansion and compressibility coefficients, respectively, with molar volume. Elements in columns 3, 6, 9, and 10 should be multiplied by the factors indicated at the column heads. (b) Correlation coefficients from the least squares analysis. Values less than 0.005 in absolute value have been set to zero.

(a)

	H	σ_H	S x 10^{-3}	V	a	b x 10^{-5}	c	d	αV x 10^{-5}	βV x 10^{-3}
ab	-3928.89	2.15	220.0	10.043	0.4520	-1.336	-1276	-3.954	27.0	16.0
pa	-5948.32	2.16	276.0	13.198	0.8030	-3.158	217	-8.151	42.0	18.0
and	-2591.72	0.52	91.4	5.152	0.2904	-1.052	-1109	-2.628	12.7	2.8
ky	-2595.89	0.51	82.3	4.415	0.3039	-1.339	-895	-2.904	11.2	1.9
jd	-3029.94	2.09	133.5	6.040	0.3011	1.014	-2239	-2.055	17.0	4.5
cor	-1675.51	0.51	50.9	2.558	0.1574	0.072	-1897	-0.988	6.4	0.9
q	-910.59	0.44	41.5	2.269	0.1044	0.607	34	-1.070	13.4	5.2
H2O	-241.81	0.02	188.8	0	0.0401	0.866	488	-0.251	0	0

(b)

	ab	pa	and	ky	jd	cor	q	H2O
ab	1.000	0.970	0.060	0.087	0.974	-0.091	0.202	0.000
pa		1.000	0.195	0.225	0.970	0.123	0.085	0.009
and			1.000	0.790	0.000	0.483	0.333	0.000
ky				1.000	0.000	0.498	0.343	0.000
jd					1.000	0.000	0.000	0.000
cor						1.000	-0.417	0.000
q							1.000	0.000
H2O								1.000

in this case $\mathbf{J} = [1\ -1\ -1]$ and $\mathbf{V}$ is the covariance matrix assembled from the uncertainties and correlations in Table 5. Setting all correlations to zero yields a diagonal covariance matrix:

$$\mathbf{V} = \begin{bmatrix} 2.15^2 & & \\ & 2.09^2 & \\ & & 0.44^2 \end{bmatrix} \text{ and } \sigma_{\Delta H} = 2.1 \text{ kJ}.$$

However, inclusion of correlations leads to:

$$\mathbf{V} = \begin{bmatrix} 2.15^2 & 4.377 & 0.191 \\ 4.377 & 2.09^2 & 0.000 \\ 0.191 & 0.000 & 0.44^2 \end{bmatrix} \text{ and } \sigma_{\Delta H} = 0.2 \text{ kJ},$$

so that although many entries in the table for enthalpy uncertainties are moderately large, the high correlations among them can lead to calculated enthalpies of reaction, and thus the calculated position of reactions, with very small errors. To put the above into context for this reaction, the uncertainies ± 2.1 kJ and ± 0.2 kJ propagate to pressure uncertainties of ± 1.2 kbar and ± 0.1 kbar respectively.

A COMPUTATIONAL NOTE

For this small worked example, the least squares solution was obtained by solving the normal equations as discussed above. However, in systems where collinearity is a major problem, as in the next paper, the normal equations route should be avoided. In such situations, the formation of $\mathbf{R}^T\mathbf{R}$, and the finding of its inverse, leads to numerical instabilities which result in severe rounding errors and the computation of meaningless regression parameters (Belsley *et al.*, 1980). Consequently, in the second paper we avoid forming $\mathbf{R}^T\mathbf{R}$ by utilizing the singular value decomposition (SVD) of $\mathbf{R} = \mathbf{USA}^T$ (Strang, 1980), in which $\mathbf{R}$ is decomposed into a matrix $\mathbf{U}$ with orthonormal columns, a diagonal matrix $\mathbf{S}$ containing the singular values, and an orthonormal matrix $\mathbf{A}$. Substituting the singular value decomposition for $\mathbf{R}$, the least squares solution becomes:

$$\mathbf{h} = (\mathbf{R}^T\mathbf{R})^{-1}\mathbf{R}^T\mathbf{b} = \mathbf{AS}^{+}\mathbf{U}^T\mathbf{b} = \mathbf{R}^{+}\mathbf{b}$$

and

$$\mathbf{V_h} = \mathbf{AS}^{-2}\mathbf{A}^T$$

where $\mathbf{R}^{+}$ is the pseudoinverse of $\mathbf{R}$. Thus the solution is obtained by working with $\mathbf{R}$ rather than its square $\mathbf{R}^T\mathbf{R}$. Weighting may be readily incorporated by working with $\mathbf{WR}$ instead of $\mathbf{R}$.

The singular value decomposition route to a least squares solution offers other advantages over and above that of numerical stability. As discussed in the next paper, the effects of collinearity can be assessed, and in this context the singular values are of diagnostic value (Belsley *et al.*, 1980).

CONCLUSIONS

We conclude that the least squares technique is a viable and worthwhile alternative to linear

programming in the solution of the internally consistent dataset problem. We are able to determine not only the consistent set of parameters which best fit the experimental data in the least squares sense, but we are also able to determine the uncertainties and correlations between the enthalpies in the dataset. We have outlined the method and illustrated it with a simple example; in the next paper we use the method on a large system and demonstrate that the results are in good agreement with the best available calorimetric data.

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