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Darken's quadratic formalism and the thermodynamics of minerals

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ABSTRACT

If a model for activity-composition relationships applies right across a binary system, then the Gibbs-Duhem equation provides a straightforward formulation for the activity coefficient of one endmember, given the formulation for the other endmember. The algebraic convenience of this may blind us to the improbability of devising models that might apply right across a system, given the obvious complexity of the energetics in even simple minerals. A model that has more realistic objectives is Darken's quadratic formalism. In this model the compositional range is divided into two terminal regions, connected by a transitional central region. In each of the terminal regions the solution behaves as a regular solution between an actual and a fictive endmember. The interaction energies in the two regions are usually very different. Whereas the subregular model involves the linear dependence of the interaction energy with composition, the quadratic formalism involves a constant interaction energy in each of the terminal regions, with the interaction energy changing only within the central region. In contrast to the subregular model, the quadratic formalism provides consistent descriptions of volume-composition relationships for binary mineral solid solutions. The inapplicability of the subregular model invalidates its use in expressing activity-composition relationships. Adoption of the quadratic formalism has important implications for geothermometry and geobarometry.

INTRODUCTION

Thermodynamic calculations involving mineral assemblages require not only thermodynamic data for endmembers, but also activity-composition (a-x) relations for minerals. The properties of the endmembers are relatively well known and easily measurable functions of temperature and pressure. In contrast, a-x relations are potentially complex, difficult to measure, and still largely unknown functions of temperature, pressure, and, particularly, composition. The compositional dependence of a-x relationships is a major problem, because an unrealistically large number of measurements is required to characterize this dependence for phases with several dimensions of compositional variation. This situation is exacerbated by the difficulty of measurement. A consequence of this is that the petrologist interested in performing calculations of equilibrium relationships for rocks has to interpolate between, or extrapolate from, a limited number of measurements. This is a difficult task, not the least because wrong decisions may invalidate the obvious choices of endmember data.

Interpolation and extrapolation of limited data require a functional form, or model, with which to analyze the data. The model exerts a critical influence on this process. As the amount of data increases, however, the choice of model becomes less and less important, particularly for interpolation, largely because the data become a test of the model. For example, in processing modern heat-capacity measurements, where typically a considerable quantity of data is available, interpolation by equation is strictly unnecessary; a smoothing spline (de Boor, 1978, p. 240–242) would do as well or better. Certainly an equation simplifies the *use* of the data, but for interpolation it does not matter what form the equation takes, as long as it fits the data satisfactorily. In fact, a number of equations may fit a given data set, but each will yield different extrapolated values. Some of the equations may be excluded from consideration because the extrapolations are obviously inappropriate. In the end, the choice of equation must be conditioned by scientific judgment based on a physical model, if only in some limiting case or cases (for the heat-capacity case, see Holland, 1980).

In processing limited data sets, the problem of functional form is much more acute. It is not unusual to encounter the case in which the number of data points and the number of adjustable parameters in the model are of the same order. Interpolation and extrapolation are, as a consequence, very model dependent. Worse, the data do not provide any test of the model, and this is often a problem in considering a-x relationships. Confidence in the veracity of a-x relationships is, of course, a prerequisite for useful geological calculations.

The purpose of this paper is to consider the form of a-x relationships and, in particular, the way in which nonideality is expressed. As a prefacing remark, it is emphasized that the thermodynamics of heterogeneous phase equilibria is envisaged as a phenomenological macroscopic description of the phases and systems involved

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(Callen, 1960; Munster, 1970). Although the use of statistical thermodynamics to formulate the thermodynamics of actual phases (e.g., as in Guggenheim, 1966) may deliver some important insights, particularly for very simple phases, it is open to doubt whether the approach is valuable for considering more complicated phases, such as most minerals. More positively, a phenomenological macroscopic approach seems preferable to a statistical one because so little is known about the fundamental behavior of minerals; further, the measurements necessary to characterize minerals properly are difficult, time-consuming, or, in the case of short-range order, often impossible to perform. In addition, if the object is to perform calculations on mineral assemblages, it is advantageous not to have to characterize minerals because their original internal arrangements will not normally survive cooling. The emphasis of this paper is on the relationships among straightforwardly measurable bulk properties of minerals as functions of composition.

BACKGROUND

The following discussion mainly concerns binary phases. Thus, there will be just one independent bulk-composition parameter, x. The solid solution will concern endmembers 1 and 2; X_1 and $X_2 = 1 - X_1$ are the mole fractions of these endmembers.

The simplest, least controversial, thermodynamic description of a binary phase divides the composition range into three regions: a Raoult's law region, a Henry's law region, and an intermediate region (Powell, 1978, p. 46–50). In the Raoult's law region, the activity a_i of endmember i approaches X_i, and the activity coefficient γ_i approaches 1 as X_i approaches 1. In the Henry's law region, a_i is proportional to X_i, i.e., γ_i is independent of X_i. The intermediate region provides a transition between the two. Raoult's law and Henry's law behavior are each a consequence of the other from the Gibbs-Duhem equation,

$$X_1 d(\ln \gamma_1) + X_2 d(\ln \gamma_2) = 0,$$

or, in the simplest integrated form,

$$\ln \gamma_2 = -\int_{\ln \gamma_{1,X_1=0}}^{\ln \gamma_{1,X_1=X_1}} \frac{X_1}{X_2}\, d(\ln \gamma_1). \tag{1}$$

Thus, if Raoult's law applies for endmember 1 for $X_1 > X_1'$, where X_1' is the compositional limit of Raoult's law behavior, then, for this region,

$$\ln \gamma_2 = -\int_{\ln \gamma_{1,X_1=0}}^{\ln \gamma_{1,X_1=X_1'}} \frac{X_1}{X_2}\, d(\ln \gamma_1) - \int_{\ln \gamma_{1,X_1=X_1'}}^{\ln \gamma_{1,X_1=X_1}} \frac{X_1}{X_2}\, d(\ln \gamma_1).$$

The second term on the right is zero because $\ln \gamma_1$ does not vary in the region $X_1' \leq X_1 \leq 1$; the first term is clearly independent of composition, as required. Given that the a-x relationships for the Raoult's law and Henry's law regions are defined, the focus of our concern is the intermediate region.

Margules in 1895 suggested that the free energy of mixing could be represented by a power series in X_2; he showed that, for Raoult's law and Henry's law to apply, the lowest-order nonzero term in the series is the one quadratic in X_2. If a quadratic approximation is employed, omitting higher-order terms in X_2, then

$$RT \ln \gamma_1 = wX_2^2, \tag{2}$$

where w is an adjustable parameter dependent on temperature and pressure, but not on composition. If Equation 2 applies over the whole compositional range, then by Equation 1

$$RT \ln \gamma_2 = -\int_0^{X_1} \frac{X_1}{X_2}(-2wX_2)\, dX_1$$
$$= wX_1^2. \tag{3}$$

Thus the a-x relationships are symmetric. Early workers showed that this quadratic approximation provides a good description of several systems of nonelectrolytes. Hildebrand showed the wider applicability of the approach. He coined the name "regular" for solutions following the quadratic approximation, requiring, in addition, that w not be a function of temperature. The attraction of making w temperature independent is that the entropy of mixing is that of an ideal solution.

As a purely empirical device, there are two major problems with the regular model of Hildebrand and others: the requirement that $w \neq f(T)$ and the assumption that the model should apply for complete binary systems, i.e., $0 \leq X \leq 1$. The first requirement is unnecessary and not restrictive. The second is, in fact, much more restrictive and not generally obeyed, as suggested in a seminal paper by Darken (1967). In his paper, Darken showed that, for various binary metallic solutions, there are three compositional regions: two terminal regions in which the quadratic approximation applies and a central region, transitional between the two terminal regions (Fig. 1). This is the basis of his quadratic formalism.

Attempted atomistic rationales of the regular solution model are inadequate. The naivety of justifying the regular model with an approach involving summing the energies of nearest-neighbor pairs is obvious when it is realized that it is the quasi-chemical model, not the regular model, that results when the necessary nonrandom distribution of nearest-neighbor pairs is included (e.g., Powell, 1983b, p. 241, 244–249). The quasi-chemical model itself is flawed in that the handling of the nonrandom distribution can only be approximate. Taking the quasi-chemical model as an approximation, the interesting limit is not that the quasi-chemical model reduces to the regular model for vanishingly small departures from ideal mixing, but that the quasi-chemical model reduces to the quadratic approximation for the terminal regions (Powell, 1983b, p. 253 and Fig. 4). This is an important observation because the quasi-chemical model is least inappropriate in the terminal regions. The same observation applies for generalizations of the quasi-chemical model, including, less obviously, multisite cases.

In summary, from empirical observations, and from limits to theoretical models, $\ln \gamma_i$ is proportional to $(1 - X_i)^2$ in the terminal regions of binary systems. In the systems considered by Darken, the terminal regions are wide and the central region very narrow. In consequence, it is possible that the quadratic formalism is more than just an empirical device, but may have a physical basis. Certainly, considering w as an interaction parameter in the quasi-chemical sense, it is reasonable to suppose that the energetics in the two terminal regions are different, possibly markedly so; for example, the sizes and shapes of sites in a mineral, under the influence of the dominant ion, may be very different in each of the terminal regions. The central region then has the simple interpretation of involving transitional energetic relationships. Darken observed that the central region often includes compositions that correspond to stable addition compounds. In the Mg-Bi system portrayed in Figure 1, Mg_3Bi_2 is a stable lower-temperature addition compound. The same appears to apply for pyrrhotite, which has a central region that includes the composition of the important low-temperature addition compound, 4*C* pyrrhotite (Powell, 1983a). For systems that show phase separation, it is reasonable to expect that the central region at higher temperature includes the position of a solvus crest, leading to a natural way of explaining solvus asymmetry.

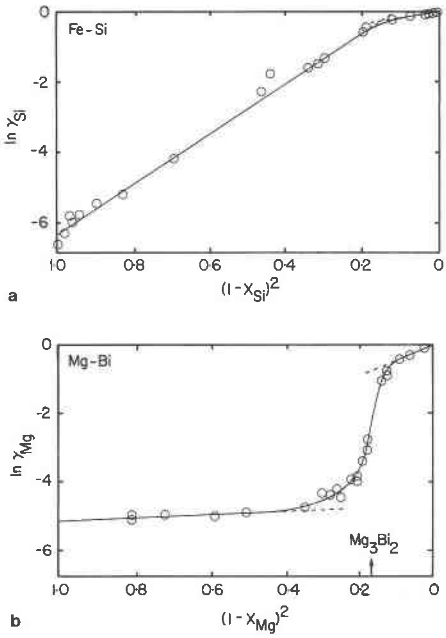


Fig. 1. (a) $\ln \gamma_{Si}$ plotted against $(1 - X_{Si})^2$ for binary Fe-Si liquid alloys at 1600°C; (b) $\ln \gamma_{Mg}$ plotted against $(1 - X_{Mg})^2$ for binary Bi-Mg liquid alloys at 700°C (from Darken, 1967). Note that in both diagrams there are two terminal regions and a transitional central region. In contrast to the central region in (a), the central region in (b) involves an inflection. The composition at the inflection is close to the composition of the lower-temperature addition compound, Mg_3Bi_2.

QUADRATIC FORMALISM

If for the terminal region including $X_1 = 1$, referred to as terminal region 1, $\ln \gamma_1$ is linear in X_2^2, then

$$RT \ln \gamma_1 = w_{12} X_2^2 \tag{4}$$

with 1 preceding 2 in the subscript of w to show that the w refers to terminal region 1. Using Equation 1 to derive $\ln \gamma_2$ involves integration from $X_1 = 0$ to the composition of interest in terminal region 1, across all of terminal region 2, all of the central region, and part of terminal region 1. If X_1' is used to denote the low-X_1 boundary of terminal region 1, then

$$RT \ln \gamma_2 = -\int_{RT \ln \gamma_{1,X_1=0}}^{RT \ln \gamma_{1,X_1=X_1'}} \frac{X_1}{X_2}\, d(\ln \gamma_1) - \int_{X_1=X_1'}^{X_1=X_1} \frac{X_1}{X_2}(-2X_2 w_{12})\, dX_1.$$

Denoting the first integral by i, then

$$RT \ln \gamma_2 = i - w_{12} X_1'^2 + w_{12} X_1^2 = I_2 + w_{12} X_1^2 \tag{5}$$

in which I_2 is not a function of composition. This equation says that the activity coefficient for endmember 2 depends on the same parameter, w_{12}, as does the activity coefficient for endmember 1, but that there is an additional constant term, I_2, involved. Note that $I_2 = 0$ only if Equation 4 applies over $0 \leq X_1 \leq 1$. For the terminal region including $X_2 = 1$, referred to as terminal region 2,

$$RT \ln \gamma_1 = I_1 + w_{21}(1 - X_1)^2 \tag{6}$$

and

$$RT \ln \gamma_2 = w_{21}(1 - X_2)^2. \tag{7}$$

Note that there is no requirement for w_{12} and w_{21} in Equations 4–7 to be related to each other, or, indeed, for them even to be of the same sign. In the terminal regions, the activity coefficient relationships are those of regular solutions, except for I_2 in Equation 5 and I_1 in Equation 6. No simple activity coefficient equation can be written for the central region. The only requirement is that the terminal regions are connected.

Combining Equations 4 and 5 for terminal region 1 with the endmember Gibbs energies, G_1 and G_2, and the entropy of mixing, S^{mix}, gives the Gibbs energy, G. For terminal region 1,

$$\begin{aligned} G &= X_1 G_1 + X_2 G_2 - TS^{mix} + X_1 w_{12}(1 - X_1)^2 \\ &\quad + X_2 w_{12}(1 - X_2)^2 + X_2 I_2 \\ &= X_1 G_1 + X_2(G_2 + I_2) - TS^{mix} + X_1 X_2 w_{12}. \end{aligned} \tag{8}$$

Similarly, for terminal region 2,

$$G = X_1(G_1 + I_1) + X_2G_2 - TS^{\mathrm{mix}} + X_1X_2w_{21}. \quad (9)$$

These equations show that Darken's quadratic formalism actually corresponds, in each of the terminal regions, to regular solutions, with each involving a real and a fictive endmember. In terminal region 1, the endmembers are 1 and a fictive endmember 2, whose Gibbs energies are G_1 and $G_2' = G_2 + I_2$, respectively; in terminal region 2, the endmembers are 2 and a fictive endmember 1, whose Gibbs energies are G_2 and $G_1' = G_1 + I_1$, respectively. Thus, Equations 4–7 can be written as, for terminal region 1,

$$\begin{aligned} RT\ln\gamma_1 &= \phantom{G_2' - G_2 +{}} w_{12}(1 - X_1)^2 \\ RT\ln\gamma_2 &= G_2' - G_2 + w_{12}(1 - X_2)^2, \end{aligned}$$

and for terminal region 2,

$$\begin{aligned} RT\ln\gamma_1 &= G_1' - G_1 + w_{21}(1 - X_1)^2 \\ RT\ln\gamma_2 &= \phantom{G_1' - G_1 +{}} w_{21}(1 - X_2)^2. \end{aligned} \quad (10)$$

Note that there need be no correlation of properties between the terminal regions. For example, there is no way of predicting w_{12} from w_{21}.

In one particular case the fictive endmembers correspond to something that can be observed. If there is a phase change, say from structure α for high X_1, to structure β for low X_1, then the above equations apply, with $G_1 = \mathrm{G}_{1\alpha}$, $G_1' = \mathrm{G}_{1\beta}$, $G_2 = \mathrm{G}_{2\beta}$, and $\mathrm{G}_2' = \mathrm{G}_{2\alpha}$, and the central region corresponds to the transformation $\alpha = \beta$. Otherwise the fictive endmembers will not be observable. For example G_2' is the Gibbs energy of pure 2, in which the energetics are the same as those applying in terminal region 1. There is a close parallel here with the fictive endmembers used in considering aqueous solutions (e.g., Powell, 1978, p. 94).

It is more clearly illustrative to consider enthalpy or volume rather than Gibbs energy. The following is formulated for volume, but the relationships apply equally to enthalpy, by replacing each V (or v) by H (or h). Given volume measurements for a solid solution, a method, preferably a graphical one, is required for evaluating the quadratic formalism and for obtaining the unknowns, which are the mixing property v_{12} or v_{21} (instead of w_{12} or w_{21}) and the volumes of the fictive endmembers, V_1' and V_2'. Following the approach of Turkdogan and Darken (1968), we start by writing V^{mix}, using x for X_1 (to emphasize that there is one independent variable in a binary system), for terminal region 1

$$V^{\mathrm{mix}} = (1 - x)(V_2' - V_2) + v_{12}x(1 - x) \quad (11a)$$

and for terminal region 2

$$V^{\mathrm{mix}} = x(V_1' - V_1) + v_{21}x(1 - x). \quad (11b)$$

For terminal region 1, dividing Equation 11a by $(1 - x)$ gives a function linear in x, with slope v_{12} and intercept at $x = 0$ of $\mathrm{V}_2' - \mathrm{V}_2$ (Turkdogan and Darken, 1968):

$$\frac{V^{\mathrm{mix}}}{1 - x} = V_2' - V_2 + v_{12}x. \quad (12a)$$

Similarly, for terminal region 2,

$$\frac{V^{\mathrm{mix}}}{x} = V_1' - V_1 + v_{21}(1 - x). \quad (12b)$$

Equation 12 is useful for processing volume and enthalpy data. The linearity required by Equation 12 allows the delineation of terminal regions.

An important V-x relationship for the subregular model is

$$\frac{V^{\mathrm{mix}}}{x(1 - x)} = v_{12}x + v_{21}(1 - x) = v_{21} + x(v_{12} - v_{21}). \quad (13)$$

This function is linear in composition. In contrast, for terminal region 1 in the quadratic formalism,

$$\frac{V^{\mathrm{mix}}}{x(1 - x)} = \frac{1}{x}(V_2' - V_2) + v_{12}, \quad (14a)$$

and for terminal region 2,

$$\frac{V^{\mathrm{mix}}}{x(1 - x)} = \frac{1}{1 - x}(V_1' - V_1) + v_{21}; \quad (14b)$$

these functions define two curved segments whose curvatures depend on $(V_2' - V_2)$ and $(V_1' - V_1)$. Whereas the subregular model implies that the interaction parameter is linearly dependent on composition over the entire range $0 \le x \le 1$, the quadratic formalism implies that the interaction parameter is *constant* in each of the terminal regions and changes only in the central region. Absence of the linear relationship for $0 \le x \le 1$ in Equation 13 precludes the general applicability of the subregular model to volume-composition relationships.

The analysis of most ion-exchange experimental data involves considering the exchange equilibrium between a fluid (f) and a binary mineral solid solution (m). For endmembers 1 and 2, the equilibrium relationship is

$$0 = \Delta G^0 + RT\ln\left(\frac{X_2}{X_1}\right)_{\mathrm{f}}\left(\frac{X_1}{X_2}\right)_{\mathrm{m}} + RT\ln\left(\frac{\gamma_2}{\gamma_1}\right)_{\mathrm{f}}\left(\frac{\gamma_1}{\gamma_2}\right)_{\mathrm{m}},$$

which is equivalent to

$$RT\ln\left(\frac{\gamma_1}{\gamma_2}\right)_{\mathrm{m}} + C = -RT\ln\left(\frac{X_2}{X_1}\right)_{\mathrm{f}}\left(\frac{X_1}{X_2}\right)_{\mathrm{m}} \quad (15)$$

in which C is a constant at a particular pressure and temperature if the activity coefficient terms for the fluid are approximately constant in the range of experimental conditions.

From the quadratic formalism (Eq. 10), for terminal region 1,

$$RT\ln\left(\frac{\gamma_1}{\gamma_2}\right) = -(G_2 - G_2') + w_{12}(1 - 2x), \qquad (16a)$$

and for terminal region 2,

$$RT\ln\left(\frac{\gamma_1}{\gamma_2}\right) = (G_1 - G_1') - w_{21}(1 - 2x). \qquad (16b)$$

If the right side of Equation 15 is plotted against composition, x, then the data should plot as two linear segments, corresponding to the terminal regions, with a transitional central region. In contrast, for the subregular model, $RT\ln(\gamma_1/\gamma_2)$ is quadratic in x for $0 \leq x \leq 1$.

VOLUME-COMPOSITION RELATIONSHIPS

Volume-composition (V-x) data are particularly useful in evaluating mixing models because these data are usually much more precise than, for example, calorimetrically determined enthalpy-composition data. Conclusions based on volume-composition data are important because the pressure dependence of $\ln a$ is related to partial molar volume, for example, in the quadratic formalism (Eq. 10) for terminal region 1, the derivative is $\partial(RT\ln a_1)/\partial P = X_2^2 v_{12}$. The formulation for activity-composition relationships when differentiated with respect to pressure must be reducible to a form consistent with volume-composition relationships. Thus, if a particular formulation of volume-composition relationships is found to be inappropriate, then this formulation cannot be used for activity-composition relationships. For example, even if activity-composition data for a system are consistent with the subregular model, this formulation is inappropriate if the volume-composition data for the system precludes the applicability of the subregular model, provided that the volume data are more precise than the activity data. Alternatively, if the quadratic formalism is well-supported by volume-composition data, any formulation reducible to the quadratic formalism will be appropriate for considering activity-composition data. Note that the subregular model is not reducible to the quadratic formalism.

Newton and Wood (1978) have observed systematic compositional dependences of molar volumes in several binary silicate mineral solid solutions, and they have accounted for these in a novel but entirely reasonable way. They noted that, in many minerals in binary systems that involve a large difference between the molar volumes of the endmembers, there are narrow regions of anomalously small volumes of mixing near the endmember with the smaller molar volume, giving way to wide regions of large excess volumes toward the endmember with the larger molar volume. Referring to this as equivalent site (ES) substitution, they ascribed this behavior to the consequences of different-sized ions mixing on the same site,

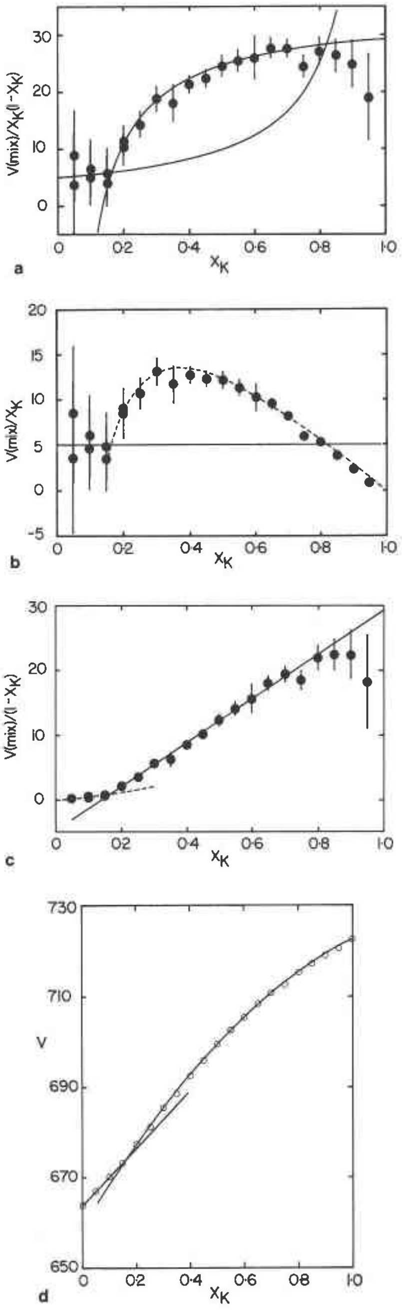


Fig. 2. Volume-composition relationships for microcline-low albite using data from Kroll et al. (1986). V refers to unit-cell ⟶ volume in Å^3. The uncertainty bars on (a–c) are for 2σ on propagated error, including the uncertainties on the volumes of the endmembers, but not including uncertainties on composition. This means that the bars are likely to be underestimates for $x < 0.05$ and $x > 0.95$. In (d), the uncertainties are less than the sizes of the symbols. Diagram (a), with reference to Eqs. 13 and 14, shows that the data cannot be described with the subregular model. Diagrams (b) and (c), with reference to Eq. 12, are used to delineate and parameterize the terminal regions; the linear segments are shown by solid lines. The solid lines in (a) and (d) and the dashed lines in (b) and (c) are calculated from the solid lines in (b) and (c). The solid lines in (b) and (c) were produced by eye, with $V_{Na} = 663.8$, $V_K' - V_K = 5$, $v_{NaK} = 0$ and $V_{Na}' - V_{Na} = -4.6$, $V_K = 722.6$, $v_{KNa} = 34$ in units of ångströms.

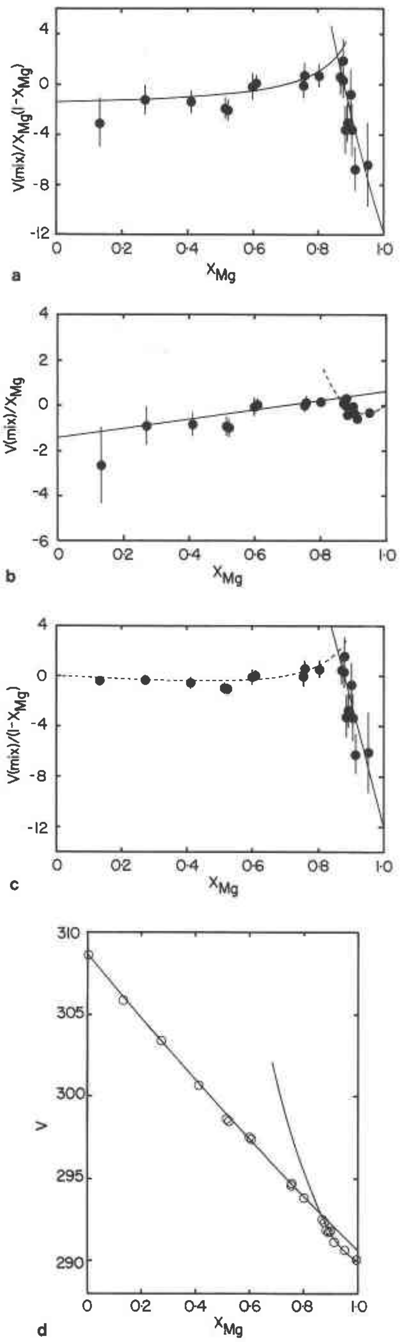


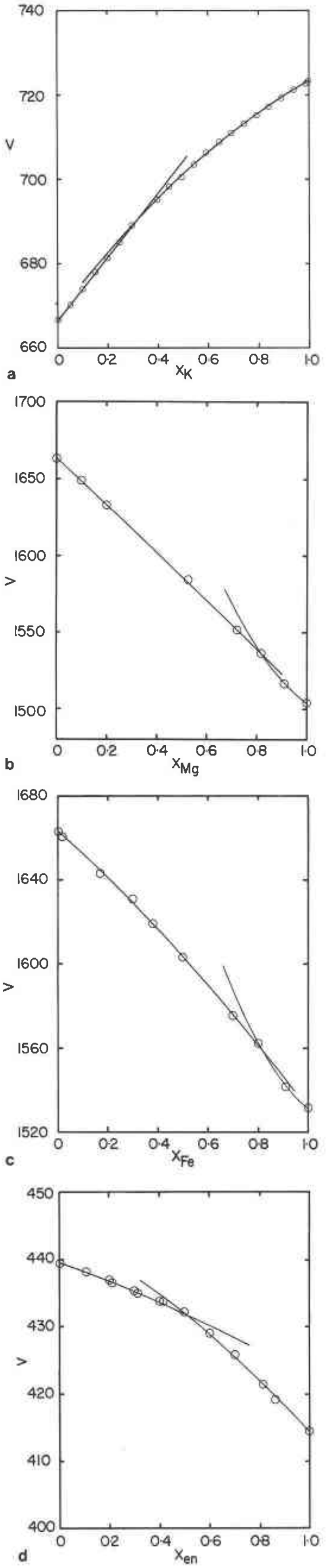
Fig. 3. Volume-composition relationships for forsterite-fayalite using data from Louisnathan and Smith (1968). See the caption for Fig. 2 for details. The parameters used to generate the lines are $V_{\mathrm{Fe}} = 308.7$, $V'_{\mathrm{Mg}} - V_{\mathrm{Mg}} = 0.6$, $v_{\mathrm{FeMg}} = -2$, and $V'_{\mathrm{Fe}} - V_{\mathrm{Fe}} = 88$, $V_{\mathrm{Mg}} = 290.1$, $v_{\mathrm{MgFe}} = -100$.

as, for example, in Fe-Ca and Mg-Ca garnet solid solutions. In other minerals, a broadly sigmoidal volume-composition dependence, referred to as nonequivalent site (NS) substitution, is ascribed to the competition of different-sized ions for different-sized sites, for example, in nepheline.

Volume-composition relationships are portrayed in various ways for microcline–low albite (using data of Kroll et al., 1986) (Fig. 2) and for forsterite-fayalite (using data of Louisnathan and Smith, 1968) (Fig. 3). Both solid solutions show typical ES behavior. Figures 2a and 3a should be viewed in relation to Equations 13 and 14. Both diagrams show that it is not possible to put a straight line through all the data as required for the subregular model, as is pointed out by Kroll et al. (1986) for their data. In fact, this is true for all systems showing ES behavior; the subregular model cannot describe such strongly asymmetric behavior. In strong contrast, the data are easily described using the quadratic formalism. Figures 2b–2c and 3b–3c should be viewed in relation to Equation 12; in both, the data show two terminal regions, and, by implication, a narrow central region. The volume-composition relationships described in this way are shown in Figures 2d and 3d. In general, for systems showing ES behavior, there is a very wide terminal region that includes the endmember with the larger molar volume and that shows ideal or small positive or negative deviations from ideality or, in the case of systems showing immiscibility, larger positive deviations from ideality. The terminal region including the endmember with the smaller molar volume is narrow and is difficult to characterize because it usually contains few measurements. An interpretation consistent with the data and also with Newton and Wood's qualitative explanation of this behavior involves strong negative deviation from ideality in this terminal region. "Ideal" is used here in relation to mixing between real and fictive endmembers; in other words, in relation to the sign of v_{ij} in Equation 11. Although not giving a unique interpretation, the simplest consistent way in which to apply the quadratic formalism to volume-composition data is to have a very narrow central region between the terminal regions, as in Figures 3d and 4d.

Whereas it is usually true that the subregular model is inappropriate for minerals that show ES behavior, the situation is less clear for minerals showing NS behavior. Broadly sigmoidal and other volume-composition relationships can often be described in terms of the subregular model within the uncertainty on the data. Diagrams like Figure 2a for such systems do not demonstrate the inapplicability of the subregular model, although they are not a convincing demonstration of it. The quadratic formalism may be a superior representation for such phases as well.

Volume-composition data for several binary mineral systems are shown in Figure 4. In Figure 4a, the position of the central region coincides with the position of a displacive transformation in this system (Kroll et al., 1986). The examples presented here support the use of the quadratic formalism for volume-composition data and, moreover, suggest that the subregular model is inappropriate. This is important because if the V-x relationships



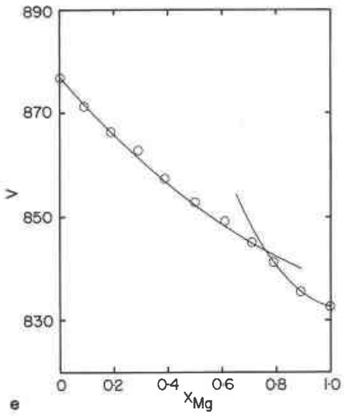


Fig. 4. Volume-composition relationships for (a) sanidine-high albite using data from Kroll et al. (1986); (b) pyrope-grossular using data from Newton et al. (1978); (c) almandine-grossular using data from Cressey et al. (1978); (d) clinoenstatite-diopside using data from Turnock et al. (1973) and Newton et al. (1979); and (e) enstatite-orthoferrosilite using data from Matsui et al. (1968). See the caption for Fig. 2 for details.

are not subregular, then it is *not possible* to express activity coefficients with subregular equations.

ENTHALPY AND ACTIVITY-COMPOSITION RELATIONSHIPS

Available enthalpy of solution-composition (H-x) data for mineral solid solutions are neither abundant nor precise enough to provide much evidence for or against the quadratic formalism or the subregular model. If enthalpy of solution measurements are obtained at intervals of 0.2 in x, then the sort of strongly asymmetric behavior found in ES minerals may not be observed. However, a recent study on grossular-almandine, where effort was concentrated on almandine-rich compositions, has delineated the expected asymmetric behavior (Fig. 5a, using data of Geiger et al., 1985). Although there are few data for the pyrope-grossular system (Fig. 5b, using data of Newton et al., 1978), the form of a description using the quadratic formalism is well defined. In both pyrope-grossular and almandine-grossular, the wide terminal regions that include grossular may involve small or zero interaction enthalpies.

Enthalpies of solution for the albite-anorthite system have been measured by Newton et al. (1980) and Carpenter et al. (1985); their results, which are plotted in Figure 6 are broadly consistent. Newton et al. used the subregular model to fit their data, but an equally satisfying description of the data is provided by the quadratic formalism (Fig. 6). Carpenter et al. provided a convincing structural interpretation of the data, involving the lower X_{an} plagioclases having the $C\bar{1}$ structure, and the higher X_{an} plagioclases having the $I\bar{1}$ structure. The quadratic formalism is still an appropriate description of data even if there is a phase transformation in the system, whereas

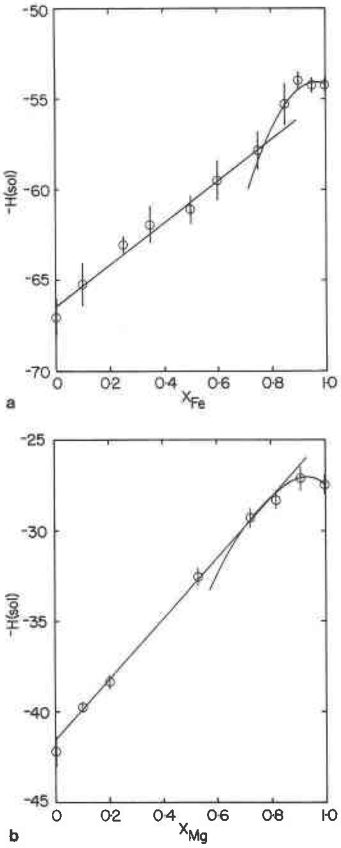


Fig. 5. Enthalpy of solution-composition relationships for (a) almandine-grossular using data from Geiger et al. (1985) and (b) pyrope-grossular using data from Newton et al. (1978). Units are kilocalories per mole. Error bars are 2σ.

the subregular model is not. The only requirement for the application of the quadratic formalism in this case is that the central region must be of zero width, involving a discontinuity corresponding to the enthalpy change of the transformation. With reference to Figure 6 and to Figure 3 of Carpenter et al. (1985), the $C\bar{1} \rightleftharpoons I\bar{1}$ transformation occurs at $0.72 \leq X_{an} \leq 0.78$. The greater the X_{an} of the transformation beyond the intersection of the lines on Figure 6, the greater is the enthalpy change of the transformation. With the uncertainties on the data, the size of this change is effectively unconstrained.

Ion-exchange experimental results have been published for a number of systems, including the plagioclase system (Orville, 1972; Blencoe et al., 1982) and the alkali feldspar system (Orville, 1963; Iiyama, 1974), both at high temperature. The plagioclase results are plotted, according to Equation 15, in Figure 7. In view of Equation 16, such a plot will consist of two linear segments, corresponding to the terminal regions, with a connecting central region. Blencoe et al. fitted these data using the subregular model; as already discussed, this is inappropriate because a phase transformation is involved in this system. The alkali feldspar results at 700°C are plotted in Figure 8. Thompson and Waldbaum (1968) and Thompson and Hovis (1979) ignored the lowest and highest X_K measurements, then fitted the remainder with the subregular model. An alternative description involving the quadratic formalism is shown on Figure 8. The position of the central region in Figures 8 and 4a is the same within experimental error and corresponds to the composition at which the displacive transformation occurs in this system. Use of the subregular model to smooth alkali feldspar solvus data (e.g., Parsons, 1978) could be positively misleading, particularly if used to predict the composition, and even the temperature, of the consolute point.

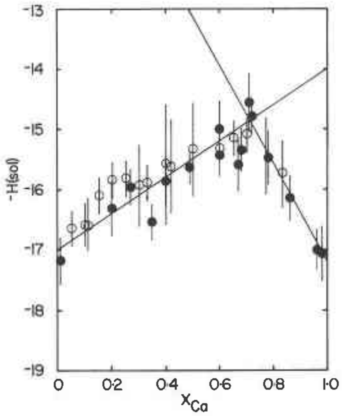


Fig. 6. High-temperature albite-anorthite enthalpy of solution-composition relationships using data from Newton et al. (1980) (open symbols) and Carpenter et al. (1985) (filled symbols). Units are kilocalories per mole. Error bars are 2σ, with a superimposed minimum of $\sigma = 0.15$. See text for discussion.

COMPUTATIONAL ASPECTS

Volume-composition and enthalpy-composition data can be easily processed to give the quadratic formalism parameters. The recommended approach is (1) to use diagrams based on Equation 12 (e.g., Figs. 2b, 2c, 3b, 3c) to determine the position of the central region and to divide the data up into two subsets, corresponding to the terminal regions, and (2) to fit these subsets for terminal region 1

$$V = X_1 V_1 + X_2 V_2' + X_1 X_2 v_{12},$$

and for terminal region 2,

$$V = X_1 V_1' + X_2 V_2 + X_1 X_2 v_{21}. \qquad (17)$$

using least squares or a variant (e.g., robust regression, Powell, 1985), with V as dependent variable, X_1, X_2, and X_1X_2 as independent variables, V_1, V_2', and v_{12} as parameters for terminal region 1, and V_1', V_2 and v_{21} as parameters for terminal region 2. It is preferable to use Equation 17 rather than Equation 12 in the regression because the calculation of V^{mix} involves V_1 and V_2; these values are usually known only as well as the other measured volumes.

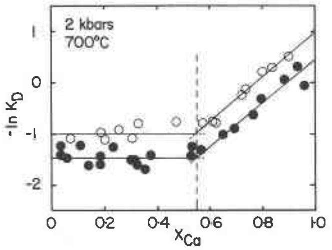


Fig. 7. Ion-exchange experimental data at 2 kbar and 700°C for high-temperature albite-anorthite solid solutions using the data of Orville (1972) (filled symbols) and Blencoe et al. (1982) (open symbols). See text for discussion.

As an example, the microcline–low albite data of Kroll et al. (1986) were processed in this way, choosing the composition $X_K = 0.175$ to divide the data into two subsets (Fig. 2). For the terminal region at high X_K using robust regression (Powell, 1985),

$$V_K = 722.35 \pm 0.38 \quad (2\sigma)$$
$$V'_{Na} = 659.21 \pm 0.50$$
$$v_{KNa} = 34.0 \pm 2.1$$

with the correlation coefficient matrix

$$\begin{bmatrix} 1.000 & 0.523 & -0.781 \\ & 1.000 & -0.874 \\ & & 1.000 \end{bmatrix},$$

and for the terminal region at low X_K,

$$V'_K = 718.9 \pm 24.6$$
$$V_{Na} = 663.80 \pm 0.10$$
$$v_{NaK} = 10.0 \pm 28.4$$

with a correlation coefficient matrix

$$\begin{bmatrix} 1.000 & -0.076 & -0.9993 \\ & 1.000 & 0.044 \\ & & 1.000 \end{bmatrix}.$$

As expected, most of the parameters for the smaller terminal region are poorly defined. However, they combine to give small uncertainties on calculated volumes where the equation is of interest.

DISCUSSION

The quadratic formalism provides a better description of volume-, enthalpy-, and activity-composition relationships than currently adopted models, in particular, the subregular model. The quadratic formalism is a very flexible model. It is, for example, able to describe the considerable asymmetry of some volume-composition relationships. This flexibility is due in part to the relatively large number of parameters needed to characterize the terminal regions. For a binary system there are four parameters: the properties of two fictive endmembers and two interaction parameters. The way in which these parameters interact controls the position of the central region, which, in turn, controls the degree and form of asymmetry of properties.

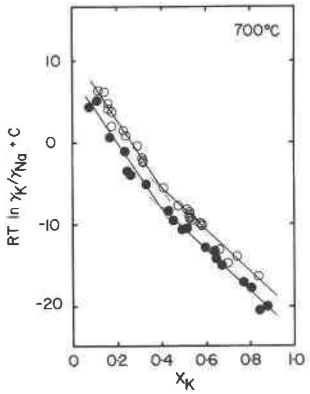


Fig. 8. Ion-exchange experimental data at 2 kbar and 700°C for sanidine–high albite solid solutions using the data of Orville (1963) (open symbols) and Iiyama (1974) (closed symbols). Units are kilojoules. See text for discussion.

It might be argued that with a four-parameter Margules expansion, with terms up to quintic in x, there would be no difficulty in describing, for example, the volume-composition relationships involved in ES behavior. However, the linearity of ln γ_i in the terminal regions in Figure 1 cannot be described by a Margules expansion. The problem with the data for minerals, even the volume data, is that it is not really sufficiently precise to allow differentiation between models. If there are substantial terminal regions with quadratic formalism properties, then a Margules expansion approach cannot be used. Regardless of this, it is overly optimistic to assume that a particular equation, for example, for activity-composition relationships, will apply throughout a system for phases as complex as minerals. It is this that makes the quadratic formalism attractive. The quadratic formalism is *the* simplest model if a formulation is not to apply over $0 \leq x \leq 1$.

The main implication for geothermometry and geobarometry is that a different geothermometric and/or geobarometric equation is required for each combination of terminal regions for the phases involved in the reaction. The Fe-Mg exchange equilibrium between olivine and garnet was studied experimentally by O'Neill and Wood (1979). In olivine, two terminal regions must be considered, for $X_{Mg} > 0.85$ and for $X_{Mg} < 0.85$ (Fig. 3). Treating the garnets as essentially ternary phases in the Ca-Mg-Fe system, Figures 4b and 4c show that there is a wide terminal region involving Ca-rich garnets, with $X_{Ca} > 0.2$. Owing to the absence of data on almandine-pyrope garnets, it is not known if ES behavior occurs in this binary system. If not, low-Ca garnets might be treated in terms of one terminal region, with the almandine-pyrope binary system considered to be a regular solution. Then, for the olivine-garnet equilibrium, four geothermometer equations are required: for olivine ($X_{Mg} >$ 0.85) + garnet ($X_{Ca} < 0.2$); for olivine ($X_{Mg} < 0.85$) +

garnet ($X_{Ca} < 0.2$); for olivine ($X_{Mg} > 0.85$) + garnet ($X_{Ca} > 0.2$); and for olivine ($X_{Mg} < 0.85$) + garnet ($X_{Ca} > 0.2$). The experimental calibration of O'Neill and Wood focused on bulk compositions that crystallized olivine ($X_{Mg} < 0.85$) and garnet ($X_{Ca} < 0.2$), so just one of the four equations can be properly calibrated. In fact, the study did include some experiments that crystallized olivines with $X_{Mg} > 0.85$ and garnets with $X_{Ca} > 0.2$, and the inclusion of these in the data processing performed by O'Neill and Wood may have degraded the analysis. Certainly it is possible that there is a change of slope in the trend of the data at $X_{Mg}^{olivine} = 0.85$ in their Figures 1–5 and also at $X_{Ca}^{garnet} = 0.2$ in their Figure 6. These changes of slope are anticipated if the quadratic formalism is used.

For any reaction involving more than one endmember from any mineral, for example, for exchange equilibria, the ΔG^0 for the reaction will always involve at least one fictive endmember. Thus for the olivine-garnet equilibrium discussed above, for olivines with $X_{Mg} > 0.85$, the geothermometric equation will involve thermodynamic data for real forsterite but fictive fayalite, whereas for olivines with $X_{Mg} < 0.85$, it will involve real fayalite but fictive forsterite. The more phases in a reaction that show nonideal behavior, the more complex is the situation, and the more care is required. For example, for garnet-orthopyroxene-plagioclase-quartz geobarometry, with two garnet endmembers involved in the reaction, it will not be sufficient to just use data from an internally consistent data set (e.g., Powell and Holland, 1985; Holland and Powell, 1985) to calculate ΔG^0. Some of the consistency problems experienced by Perkins and Chipera (1985) may be removed by using the quadratic formalism; certainly the analysis of the thermodynamics of garnet solid solutions by Ganguly and Saxena (1984) and Wood and Holloway (1984) will need substantial re-evaluation.

Adoption of the quadratic formalism has an important bearing on future experimental work. Experiments will be needed to calibrate all the terminal regions of interest because it is not possible to extrapolate from one terminal region to another. Similarly, application of a geothermometric and/or a geobarometric equation for an inappropriate combination of terminal regions should be recognized as being dangerous, and if central regions are involved, a calculation should be bracketed by application of the equations for adjacent terminal regions.

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