

Application of the Darken equation to mineral solid solutions with variable degrees of order-disorder

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ABSTRACT

A method is outlined for application of the Darken equation to thermodynamic solutions characterized by both compositional and ordering variables. The method is simple and may be readily implemented by computer software packages designed to perform symbolic calculus and algebra.

INTRODUCTION

The mathematical expression that relates mole fraction (X) derivatives of the molar Gibbs energy (\hat{G}) to chemical potentials of solution components (μ) was first proposed by Darken and Gurry (1953). They derived an expression applicable to binary solutions and proposed the multi-component relation

$$\mu_i = \hat{G} + (1 - X_i) \left(\frac{\partial \hat{G}}{\partial X_i} \right)_{X_{\alpha}, \beta \neq i} \quad (1)$$

that generalizes the binary result with the geometrical construct known as the pseudo-binary section. A pseudo-binary is defined by focusing on the variation of the mole fraction of the i th component, from zero to unity, along a compositional join given by constant mole-fraction ratios of all other solution components. Equation 1 is arguably the most important relation in the whole of the thermodynamic theory of solutions. It has come to be known as the Darken equation.

Application of Equation 1 to simple solutions of two, three, or four components is the subject of elementary texts in solution theory. Complex solution models for rock-forming minerals, however, often generate expressions for the molar Gibbs energy that do not lend themselves to direct evaluation using Equation 1. The difficulty arises through the choice of independent variables in the formulation of the expression for the Gibbs energy. Conceptually, it is often convenient to separate compositional effects in a mineral solid-solution series from those effects that describe the extent of cation ordering among various sites at a given bulk composition (Thompson, 1969, 1970). For example, in orthopyroxene solid solutions along the Fe^{2+} -Mg binary, one might focus on the composition of the pyroxene separately from the extent of Fe^{2+} -Mg cation ordering between the M1 and M2 sites. Such considerations give rise to expressions for the molar Gibbs energy of solution of the general functional form

$$\hat{G} = \hat{G}(y_2, y_3, \dots, y_n, s_1, s_2, \dots, s_m), \quad (2)$$

where y_2 through y_n denote independent compositional parameters and s_1 through s_m refer to ordering parameters of the solid-solution series. Expressions of this type have been developed for rock-forming minerals by Davidson and Lindsley (1985, pyroxenes), Ghiorso (1990, rhombohedral oxides), Hill and Sack (1987, spinels), Sack (1980, olivines and orthopyroxenes; 1982, spinels) and Sack and Ghiorso (1989, olivines and orthopyroxenes). The molar Gibbs energy formulation embodied in Equation 2 is equivalent to one expressed in terms of a linearly independent set of $n + m$ thermodynamic components

$$\hat{G} = \hat{G}(X_1, X_2, \dots, X_{n+m}). \quad (3)$$

Though the latter definition for \hat{G} can readily be inserted into Equation 1 for evaluation of the $n + m$ end-member chemical potentials, the expression for \hat{G} generated in practice (Eq. 2) cannot.

A general method is developed for evaluating Equation 1 directly, utilizing the molar Gibbs-energy parameterization given by Equation 2. The method is amenable to automated symbolic computation (e.g., Wolfram, 1988) and is consequently applicable to expressions for the molar Gibbs energy of arbitrary complexity.

Derivation and examples

We will develop the method by first examining a simple application involving one ordering parameter in a three-component solution. Consider solid solutions in the system FeTiO_3 - Fe_2O_3 . There are three end-member thermodynamic components in this solid-solution series. We take these to be Fe_2O_3 with the hematite structure (Hm), FeTiO_3 with the fully ordered low-temperature ilmenite structure (O-II) and FeTiO_3 with the completely disordered hematite structure (D-II). Alternatively, the molar Gibbs energy of this system can be formulated using a compositional variable, y , which refers to the bulk mole fraction of FeTiO_3 in solution, and an ordering variable, s , which denotes the structure type at a given bulk composition. For the hematite structure type s is zero, and s is equal to y for the ilmenite structure type. We may then

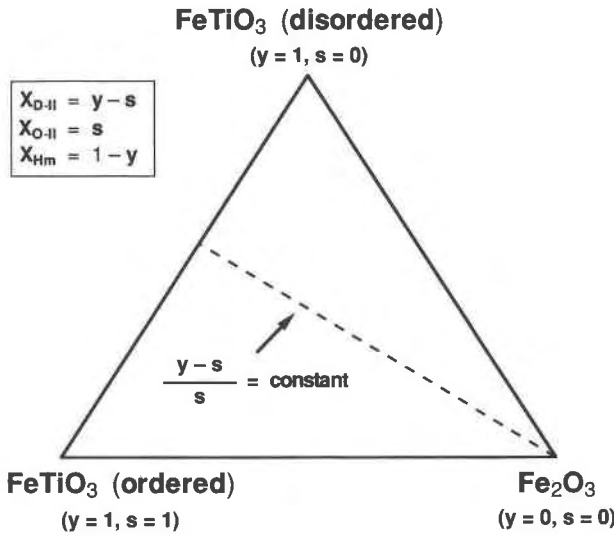


Fig. 1. Illustration of the dependency of compositional and ordering variables along the pseudo-binary join appropriate for the evaluation of the chemical potential of Fe_2O_3 in the system FeTiO_3 - Fe_2O_3 .

write equivalent definitions

$$\begin{aligned}\hat{G} &= \hat{G}(y, s) \\ &= \hat{G}(X_{\text{Hm}}, X_{\text{O-II}}, X_{\text{D-II}})\end{aligned}\quad (4)$$

following Equations 2 and 3, and obtain an expression for the chemical potential of Fe_2O_3 (with the hematite structure) by writing Equation 1 as

$$\mu_{\text{Hm}} = \hat{G} + (1 - X_{\text{Hm}}) \left(\frac{\partial \hat{G}}{\partial X_{\text{Hm}}} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} \quad (5)$$

We proceed to evaluate Equation 5 by recognizing that the total derivative of \hat{G} is given by

$$d\hat{G} = \frac{\partial \hat{G}}{\partial y} dy + \frac{\partial \hat{G}}{\partial s} ds, \quad (6)$$

and that the component mole fractions appearing in Equation 5 have definitions in terms of the preferred set of composition and ordering variables

$$\begin{aligned}X_{\text{Hm}} &= f_{\text{Hm}}(y, s) = 1 - y \\ X_{\text{O-II}} &= f_{\text{O-II}}(y, s) = s \\ X_{\text{D-II}} &= f_{\text{D-II}}(y, s) = y - s.\end{aligned}\quad (7)$$

It should be noted that the partial derivatives in Equation 6 are evaluated holding all other variables in the expression for \hat{G} constant. This is the usual method of partial differentiation and will be denoted below by the absence of parentheses about the derivative term. Substitution of Equation 6 into Equation 5 results in

$$\mu_{\text{Hm}} = \hat{G} + y \frac{\partial \hat{G}}{\partial y} \left(\frac{\partial y}{\partial X_{\text{Hm}}} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} + y \frac{\partial \hat{G}}{\partial s} \left(\frac{\partial s}{\partial X_{\text{Hm}}} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} \quad (8)$$

This expression is convenient, in that the burden of evaluating the pseudo-binary derivatives has been transferred away from the molar Gibbs-energy formulation. This transformation allows the derivatives of \hat{G} to be determined using automated computer algorithms in symbolic calculus and algebra—a necessity if \hat{G} refers to a model for solid solutions of even moderate complexity. Thus it remains that the pseudo-binary mole-fraction derivatives in Equation 8 be obtained. It is convenient to construct these derivatives in reference to Figure 1. The first expression in Equation 7 may be differentiated with respect to y and s to generate the following identities

$$\begin{aligned}\left(\frac{\partial X_{\text{Hm}}}{\partial y} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} &= \left(\frac{\partial(1-y)}{\partial y} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} = -1 \\ \left(\frac{\partial X_{\text{Hm}}}{\partial s} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} &= \left(\frac{\partial(1-y)}{\partial s} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} = - \left(\frac{\partial y}{\partial s} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}},\end{aligned}\quad (9)$$

where it must be understood that y and s no longer vary independently when attention is restricted to the pseudo-binary (see Fig. 1). This dependency emerges by differentiating the constant mole fraction ratio

$$d \left(\frac{X_{\text{O-II}}}{X_{\text{D-II}}} \right) = d \left(\frac{s}{y-s} \right) = 0, \quad (10)$$

which results in the relation

$$\frac{(y-s) - s \left[\left(\frac{\partial y}{\partial s} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} - 1 \right]}{(y-s)^2} = 0, \quad (11)$$

and the identity

$$\left(\frac{\partial y}{\partial s} \right)_{\substack{X_{\text{O-II}} \\ X_{\text{D-II}}}} = \frac{y}{s}. \quad (12)$$

Substitution of Equations 12 and 9 into Equation 8 results in an expression for the desired chemical potential in terms of simple partial derivatives in the preferred set of compositional and ordering variables

$$\mu_{\text{Hm}} = \hat{G} - y \frac{\partial \hat{G}}{\partial y} - s \frac{\partial \hat{G}}{\partial s}. \quad (13)$$

A general procedure may be formulated upon which this simple example is based. Given Equation 2 as a working definition of the molar Gibbs function, the total derivative of \hat{G} may be written:

$$d\hat{G} = \sum_{j=2}^n \frac{\partial \hat{G}}{\partial y_j} dy_j + \sum_{j=1}^m \frac{\partial \hat{G}}{\partial s_j} ds_j, \quad (14)$$

from which the partial derivative appropriate for evaluation of Equation 1 may be constructed:

$$\left(\frac{\partial \hat{G}}{\partial X_i} \right)_{\substack{X_a \\ X_b}} = \sum_{j=2}^n \frac{\partial \hat{G}}{\partial y_j} \left(\frac{\partial y_j}{\partial X_i} \right)_{\substack{X_a \\ X_b}} + \sum_{j=1}^m \frac{\partial \hat{G}}{\partial s_j} \left(\frac{\partial s_j}{\partial X_i} \right)_{\substack{X_a \\ X_b}} \quad (15)$$

As in Equation 6, the Gibbs energy derivatives in Equation 15 are taken without imposing ratio constraints. The pseudo-binary derivatives in Equation 15 may be evaluated by recognizing that each of the $n + m$ component mole fractions can be expressed as a function of the preferred set of composition and ordering variables,

$$X_\alpha = f_\alpha(y_2, y_3, \dots, y_n, s_1, s_2, \dots, s_m), \quad (16)$$

and that the pseudo-binary constraints enforce $n + m - 2$ linearly independent first-order differential equations relating these functions

$$f_\beta df_\alpha - f_\alpha df_\beta = 0. \quad (17)$$

This is because there are only $n + m - 2$ independent mole-fraction ratios that fix the orientation of the pseudo-binary section. In practical terms, these ratios may be specified by selecting α arbitrarily (as long as α is not taken to be equivalent to i) and allowing β to range over all possible values, 1 to $n + m$, except i and α . The total derivatives for f_α and f_β in Equation 17 may be expressed by the usual expansion in terms of the preferred set of composition and ordering variables. Substitution for df_α and df_β results in

$$f_\beta \left(\sum_{k=2}^n \frac{\partial f_\alpha}{\partial y_k} dy_k + \sum_{k=1}^m \frac{\partial f_\alpha}{\partial s_k} ds_k \right) - f_\alpha \left(\sum_{k=2}^n \frac{\partial f_\beta}{\partial y_k} dy_k + \sum_{k=1}^m \frac{\partial f_\beta}{\partial s_k} ds_k \right) = 0. \quad (18)$$

There are $n + m - 2$ linearly independent statements of Equation 18. Treating this set of equations as a system allows the definition of $n + m - 2$ unknowns. These may be specified by selecting an arbitrary variable, say, y_2 , for convenience, and transforming the total derivatives in Equation 18 into partial derivatives subject to the relevant pseudo-binary constraints. From Equation 18 we obtain

$$\sum_{k=3}^n \left(f_\beta \frac{\partial f_\alpha}{\partial y_k} - f_\alpha \frac{\partial f_\beta}{\partial y_k} \right) \left(\frac{\partial y_k}{\partial y_2} \right) \frac{X_\alpha}{X_\beta} + \sum_{k=1}^m \left(f_\beta \frac{\partial f_\alpha}{\partial s_k} - f_\alpha \frac{\partial f_\beta}{\partial s_k} \right) \left(\frac{\partial s_k}{\partial y_2} \right) \frac{X_\alpha}{X_\beta} = - \left(f_\beta \frac{\partial f_\alpha}{\partial y_2} - f_\alpha \frac{\partial f_\beta}{\partial y_2} \right), \quad (19)$$

which provides a system of $n + m - 2$ equations in the same number of constraint-derivative unknowns of the pseudo-binary. As we have specified linearly independent thermodynamic components, the system of equations (Eq. 19) can always be inverted (symbolically of course) to solve for the ratio derivatives. It should be apparent that all dependent derivatives may be defined from those obtained by solution of Equation 19, i.e.,

$$\left(\frac{\partial s_{k1}}{\partial y_{k2}} \right) \frac{X_\alpha}{X_\beta} = \left(\frac{\partial s_{k1}}{\partial y_2} \right) \frac{X_\alpha}{X_\beta} \left(\frac{\partial y_2}{\partial y_{k2}} \right) \frac{X_\alpha}{X_\beta}. \quad (20)$$

Equations 19 and 20 permit evaluation of the pseudo-binary constraint derivatives in Equation 15, which consequently provides a definition for the i th chemical potential upon substitution into Equation 1.

To illustrate the aspects of the general method that arise through consideration of more than three components, we generalize the example developed above to include the components MgTiO_3 with the fully ordered (ilmenite) structure (O-Gk) and MgTiO_3 with the fully disordered (hematite) structure (D-Gk). Taking the compositional variable z to denote the bulk mole fraction of MgTiO_3 and t to refer to the state of Mg-Ti order-disorder, Equations 2 and 3 become

$$\begin{aligned} \hat{G} &= \hat{G}(y, z, s, t) \\ &= \hat{G}(X_{\text{Hm}}, X_{\text{O-II}}, X_{\text{D-II}}, X_{\text{O-Gk}}, X_{\text{D-Gk}}). \end{aligned} \quad (21)$$

Focusing for illustrative purposes once again on the chemical potential of hematite, we see that Equation 1 may be written

$$\mu_{\text{Hm}} = \hat{G} + (1 - X_{\text{Hm}}) \left(\frac{\partial \hat{G}}{\partial X_{\text{Hm}}} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}}, \quad (22)$$

where the three mole-fraction ratios that define the pseudo-binary constraint have been explicitly stated. For this example, Equation 16 becomes

$$\begin{aligned} X_{\text{Hm}} &= f_{\text{Hm}}(y, z, s, t) = 1 - y - z \\ X_{\text{O-II}} &= f_{\text{O-II}}(y, z, s, t) = s \\ X_{\text{D-II}} &= f_{\text{D-II}}(y, z, s, t) = y - s \\ X_{\text{O-Gk}} &= f_{\text{O-Gk}}(y, z, s, t) = t \\ X_{\text{D-Gk}} &= f_{\text{D-Gk}}(y, z, s, t) = z - t. \end{aligned} \quad (23)$$

Equation 22 may now be expanded with the aid of Equation 15 and the definition for the mole fraction of hematite (Eq. 23) to yield the expression

$$\begin{aligned} \mu_{\text{Hm}} &= \hat{G} + (y + z) \frac{\partial \hat{G}}{\partial y} \left(\frac{\partial y}{\partial X_{\text{Hm}}} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}} \\ &+ (y + z) \frac{\partial \hat{G}}{\partial s} \left(\frac{\partial s}{\partial X_{\text{Hm}}} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}} \\ &+ (y + z) \frac{\partial \hat{G}}{\partial z} \left(\frac{\partial z}{\partial X_{\text{Hm}}} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}} \\ &+ (y + z) \frac{\partial \hat{G}}{\partial t} \left(\frac{\partial t}{\partial X_{\text{Hm}}} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}}. \end{aligned} \quad (24)$$

Evaluation of Equation 24 requires expressions for the pseudo-binary constraint derivatives. Differentiating the function f_{Hm} with respect to y , z , s , and t results in

$$\left(\frac{\partial X_{\text{Hm}}}{\partial y} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}} = -1 - \left(\frac{\partial z}{\partial y} \right) \frac{X_{\text{O-II}} X_{\text{O-II}} X_{\text{O-II}}}{X_{\text{D-II}} X_{\text{O-Gk}} X_{\text{D-Gk}}}$$

$$\begin{aligned}
\left(\frac{\partial X_{\text{Hm}}}{\partial s}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= -\left(\frac{\partial y}{\partial s}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} \\
&\quad - \left(\frac{\partial z}{\partial s}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} \\
\left(\frac{\partial X_{\text{Hm}}}{\partial z}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= -\left(\frac{\partial y}{\partial z}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} - 1 \\
\left(\frac{\partial X_{\text{Hm}}}{\partial t}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= -\left(\frac{\partial y}{\partial t}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} \\
&\quad - \left(\frac{\partial z}{\partial t}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}}. \quad (25)
\end{aligned}$$

We now utilize Equation 19 to construct three independent linear equations that relate derivatives of z , s , and t with respect to y along the pseudo-binary section:

$$\begin{aligned}
y \left(\frac{\partial s}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= s \\
t \left(\frac{\partial s}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} - s \left(\frac{\partial t}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= 0 \\
-s \left(\frac{\partial z}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} + (z - t) \\
\cdot \left(\frac{\partial s}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} + s \left(\frac{\partial t}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= 0. \quad (26)
\end{aligned}$$

Solution of Equation 26 yields

$$\begin{aligned}
\left(\frac{\partial z}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{z}{y} \\
\left(\frac{\partial s}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{s}{y} \\
\left(\frac{\partial t}{\partial y}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{t}{y}, \quad (27)
\end{aligned}$$

where the remaining dependent constraint derivatives are obtained by application of Equation 20:

$$\begin{aligned}
\left(\frac{\partial z}{\partial s}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{z}{s} \\
\left(\frac{\partial z}{\partial t}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{z}{t} \\
\left(\frac{\partial s}{\partial t}\right)_{\frac{X_{\text{O-II}}}{X_{\text{D-II}}}, \frac{X_{\text{O-II}}}{X_{\text{O-Gk}}}, \frac{X_{\text{O-II}}}{X_{\text{D-Gk}}}} &= \frac{s}{t}. \quad (28)
\end{aligned}$$

Substitution of Equations 28, 27, and 25 into Equation 24 yields an expression for the chemical potential of hematite

$$\begin{aligned}
\mu_{\text{Hm}} = \hat{G} + (y + z) \frac{\partial \hat{G}}{\partial y} \left(\frac{1}{-1 - \frac{z}{y}} \right) \\
+ (y + z) \frac{\partial \hat{G}}{\partial s} \left(\frac{1}{-\frac{y}{s} - \frac{z}{s}} \right) \\
+ (y + z) \frac{\partial \hat{G}}{\partial z} \left(\frac{1}{-\frac{y}{z} - 1} \right) \\
+ (y + z) \frac{\partial \hat{G}}{\partial t} \left(\frac{1}{-\frac{y}{t} - \frac{z}{t}} \right), \quad (29)
\end{aligned}$$

which simplifies to a relation in the form that we set out to obtain

$$\mu_{\text{Hm}} = \hat{G} - y \frac{\partial \hat{G}}{\partial y} - s \frac{\partial \hat{G}}{\partial s} - z \frac{\partial \hat{G}}{\partial z} - t \frac{\partial \hat{G}}{\partial t}, \quad (30)$$

Equation 30, or the generalized equivalent obtained by applying Equations 14–20 to Equation 1, holds for whatever functional form is adopted for \hat{G} .

SUMMARY

The advantage of the procedure outlined above is that it can be accommodated by software packages (e.g., Wolfram, 1988) that perform symbolic calculus and algebra on relatively small computer systems (Mac II or the equivalent). Chemical potentials may be constructed from expressions for the molar Gibbs energy of solution with an ease that allows the exploration of a wide spectrum of theoretical relations in a short period of time. Attention is focused less on the algebra and more on the theoretical and quantitative constraints. Even for systems with a small number of components, analyzed with pencil and paper, reduction of the Darken equation into a form relieved of its pseudo-binary constraints is useful and in application is much less subject to manipulative error.

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REFERENCES CITED

- Darken, L.S., and Gurry, R.W. (1953) Physical chemistry of metals, 535 p. McGraw Hill, New York.
- Davidson, P.M., and Lindsley, D.H. (1985) Thermodynamic analysis of quadrilateral pyroxenes. Part I. Derivation of the ternary non-convergent site disorder model. Contributions to Mineralogy and Petrology, 91, 383–389.
- Ghiorsso, M.S. (1990) Thermodynamic properties of hematite-ilmenite-geikielite solid solutions. Contributions to Mineralogy and Petrology, in press.

- Hill, R.L., and Sack, R.O. (1987) Thermodynamic properties of Fe-Mg titaniferous magnetite spinels. *Canadian Mineralogist*, 25, 443-464.
- Sack, R.O. (1980) Some constraints on the thermodynamic mixing properties of Fe-Mg orthopyroxenes and olivines. *Contributions to Mineralogy and Petrology*, 71, 257-269.
- (1982) Spinels as petrogenetic indicators: Activity-composition relations at low pressures. *Contributions to Mineralogy and Petrology*, 79, 169-182.
- Sack, R.O., and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: Thermochemistry of minerals in the system Mg_2SiO_4 - Fe_2SiO_4 - SiO_2 . *Contributions to Mineralogy and Petrology*, 102, 41-68.
- Thompson, J.B., Jr. (1969) Chemical reactions in crystals. *American Mineralogist*, 54, 341-375.
- (1970) Chemical reactions in crystals: Corrections and clarification. *American Mineralogist*, 55, 528-532.
- Wolfram, S. (1988) *Mathematica. A system for doing mathematics by computer*, 749 p. Addison-Wesley Publishing Company, New York.

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