

Phase equilibria in the system MgO-MgF₂-SiO₂-H₂OCLARENCE J. DUFFY¹ AND HUGH J. GREENWOOD*Department of Geological Sciences, University of British Columbia
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Abstract

Unit-cell parameters as functions of mole fraction fluoro-endmember have been determined for clinohumite, chondrodite, norbergite, brucite, and sellaite. In addition, the *d* spacing for the (060) peak of talc was determined as a function of mole fraction fluoro-talc. Unit-cell parameters for the phase intermediate sellaite are

$a = 10.123$, $b = 4.6861$, $c = 3.0780A$ when coexisting with periclase and

$a = 10.097$, $b = 4.6812$, $c = 3.0738A$ when coexisting with sellaite.

From these X-ray data the compositions of coexisting phases have been determined in forty hydrothermal experiments that yielded information on eighteen different chemical equilibria. These data, combined with phase equilibrium and calorimetric data from the literature, have been treated by the method of least squares to produce a thermodynamic model for the system. The derived endmember Gibbs energies of formation from the components MgO, MgF₂, SiO₂, H₂O at 1023 K and 1 bar are in cal mol⁻¹ $\Delta G_{HB}^{\circ} = 15538$, $\Delta G_{FB}^{\circ} = 8456$, $\Delta G_{HS}^{\circ} = 44092$, $\Delta G_{HN}^{\circ} = 5333$, $\Delta G_{FN}^{\circ} = -15721$, $\Delta G_{HCh}^{\circ} = -12031$, $\Delta G_{FCh}^{\circ} = -31161$, $\Delta G_{HCl}^{\circ} = -41347$, $\Delta G_{FCI}^{\circ} = -58853$, $\Delta G_{HTc}^{\circ} = -8509$, $\Delta G_{FTc}^{\circ} = -2086$, $\Delta G_{Fo}^{\circ} = -14249$, $\Delta G_{En}^{\circ} = -7566$. Computed equilibria based upon these Gibbs energies and related excess parameters combined with entropies and heat capacities are in good agreement with data on natural assemblages.

Introduction

The system MgO-MgF₂-SiO₂-H₂O is in many respects an ideal system for experimental study. High-purity starting materials are readily available. There are no oxidation-reduction problems. Phase equilibrium and calorimetric data are abundant on important subsystems. Synthesis experiments have been carried out on the solid solution phases (Van Valkenburg, 1955, 1961; Crane and Ehlers, 1969). A basis for theoretical treatment of such systems has been given by Thompson (1967) and Muan (1967).

This study combines new experimental data on multiphase equilibria in the system with available data to form an overdetermined system of equations which describe experimentally-observed chemical equilibria. The least-squares solution of these equations is presented as a model for chemical equilibrium in the system under a wide range of conditions.

Naturally-occurring equilibria that can be represented by the model have received little attention in the literature. This is more probably due to the difficulty of obtaining fluorine analyses than to the scarcity of suitable bulk compositions. What information does exist agrees well with the model.

Symbols and units

The symbols used in this paper follow as closely as practicable the usage recommended by McGlashan (1970). Additional symbols are those in common use in the geologic literature. A list of symbols and corresponding units is given in Table 1. Table 2 lists the symbols and formula units used for the various chemical compounds encountered.

Experimental methods

Apparatus

Experiments were conducted by enclosing reagent-grade chemicals in sealed noble-metal capsules and

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Appendix 2

Formulation of the Least Square Problem

Table 12 lists eighteen chemical equilibria that have been used to constrain the thermochemical quantities for the phases in this system. These equations can be split into several classes, each having an equation of a general form. There follows a derivation of each of these general equations and remarks on any simplifying assumptions that have been made.

Equilibria [2] to [7] represent fluorine hydroxyl exchange between two solid solution phases, C and D. In equilibrium composition space these equilibria are represented by tie lines between coexisting solid solution phases. The basic equation describing such equilibria is given by

$$[20] \quad \mu_{\text{HC}} + \mu_{\text{FD}} = \mu_{\text{HD}} + \mu_{\text{FC}}$$

From equation [20] it follows that

$$[21] \quad \Delta G_{\text{HC}} + \Delta G_{\text{FD}} = \Delta G_{\text{HD}} + \Delta G_{\text{FC}}$$

It should be noted that these ΔG 's refer to the species in the solid solution and not to pure endmembers. ΔG may be reduced to a more tractable form through use of an activity term such that

$$[22] \quad \Delta G = \Delta G^* + RT \ln a$$

Referring to a standard state of 1023 K and 1 bar

$$[23] \quad \Delta G = \Delta G^{\circ} + \Delta V^{\circ}(\underline{P} - 1) - \Delta S^{\circ}(T - 1023) + RT \ln a .$$

This equation is an approximation assuming ΔV and ΔS to be constant over the

range of pressure and temperature considered. The approximation is useful because variation ΔV over the pressure and temperature range of interest is small and variation for the several species involved in a given equilibria may be expected to cancel each other to a large degree. The approximation that $\Delta S^T = \Delta S^\circ$ is adequate because all of the data for these equilibria were collected within five K of 1023 K.

Combining equations [21] and [23] results in

$$[24] \quad \Delta G_R^\circ + \Delta V_R^\circ(P - 1) - \Delta S_R^\circ(T - 1023) + RT \ln \left\{ \frac{(a_{FC} a_{HD})}{(a_{HC} a_{FD})} \right\} = 0.$$

Equilibrium [8] is similar to equilibria [2] through [7] except that it represents an exchange equilibrium between a solid solution and the vapor phase. For equilibrium [8]

$$[25] \quad \mu_{HC} + 2\mu_{HF} = \mu_{FC} + 2\mu_{H_2O}.$$

Following a development parallel to that leading to equation [24], and noting that for volatile species

$$[26] \quad \Delta G = \Delta G^\circ - \Delta S^\circ(T - 1023) + RT \ln \left(\frac{f_{T,P}}{f^T, 1} \right)$$

and making the assumption that $\frac{f_{T,P}}{f^T, 1} = 1$ equation [25] becomes

$$[27] \quad \Delta G_R^\circ - \Delta V_{\text{solids},R}^\circ(P - 1) - \Delta S_R^\circ(T - 1023) + RT \ln \left(\frac{a_{FC}}{a_{HC}} \right) \\ + 2RT \ln \left(\frac{f_{H_2O}}{f_{HF}} \right) = 0.$$

Note that equation [27] contains the same approximation regarding constant ΔV_{solids} and ΔS as equation [24]. Equation [27] involves two volatile species so that the assumption of constant ΔS is somewhat less satisfactory in equation

[27], but over five K the error is still trivial.

Equilibria [9] to [17] may be written in the form

$$[28] \quad \nu_{\text{HC}}^{\text{HC}} + \nu_{\text{HD}}^{\text{HD}} + \nu_{\text{HE}}^{\text{HE}} + \nu_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} = 0.$$

From this it follows that

$$[29] \quad \nu_{\text{HC}}^{\mu\text{HC}} + \nu_{\text{HD}}^{\mu\text{HD}} + \nu_{\text{HE}}^{\mu\text{HE}} + \nu_{\text{H}_2\text{O}}^{\mu\text{H}_2\text{O}} = 0.$$

or

$$[30] \quad \nu_{\text{HC}}^{\Delta G_{\text{HC}}} + \nu_{\text{HD}}^{\Delta G_{\text{HD}}} + \nu_{\text{HE}}^{\Delta G_{\text{HE}}} + \nu_{\text{H}_2\text{O}}^{\Delta G_{\text{H}_2\text{O}}} = 0.$$

In equilibria [9] through [13] all data are within five K of 1023 K, but for equilibria [14] through [17] data are available at substantially different temperatures. Consequently it is necessary to include the heat capacity terms for reactants and products. Thus for solids

$$[31] \quad \Delta \underline{G} = \Delta \underline{G}^\circ + \Delta \underline{V}^\circ (\underline{P} - 1) - \Delta \underline{S}^\circ (\underline{T} - 1023) + \int_{1023}^{\underline{T}} \frac{\Delta \underline{C} dT}{1023} - \underline{T} \int_{1923}^{\underline{T}} \frac{(\Delta \underline{C}/\underline{T}) dT}{1923} \\ + R \underline{T} \ln a.$$

For H_2O

$$[32] \quad \Delta \underline{G}_{\text{H}_2\text{O}} = R \underline{T} \ln \left(\frac{f_{\text{H}_2\text{O}}^{\underline{T}, \underline{P}}}{f_{\text{H}_2\text{O}}^{\underline{T}, 1}} \right).$$

The rather simple form of equation [32] is due to H_2O being one of the reference compounds for the system. For this reason $\Delta \underline{G}_{\text{H}_2\text{O}}^* = 0$ by definition. Combining equations [30], [31], and [32] and assuming $\frac{f_{\text{H}_2\text{O}}^{\underline{T}, 1}}{f_{\text{H}_2\text{O}}^{\underline{T}, 1}} = 1$ gives

$$\begin{aligned}
 [33] \quad & \Delta \underline{G}_{\underline{R}}^{\circ} + \Delta \underline{V}_{\underline{\text{solids}}, \underline{R}}^{\circ} (\underline{P} - 1) - \Delta \underline{S}_{\underline{R}}^{\circ} (\underline{T} - 1023) + \int_{1023}^{\underline{T}} \underline{\Delta C}_{\underline{R}} d\underline{T} - \underline{T} \int_{1023}^{\underline{T}} (\underline{\Delta C}_{\underline{R}} / \underline{T}) d\underline{T} \\
 & + \underline{RT} (\nu_{\underline{HC}} \ln a_{\underline{HC}} + \nu_{\underline{HD}} \ln a_{\underline{HD}} + \nu_{\underline{HE}} \ln a_{\underline{HE}} + \nu_{\underline{H_2O}} \ln f_{\underline{H_2O}}) = 0.
 \end{aligned}$$

For equilibria [9] through [13], an adequate approximation to equation [33] may be obtained by deleting the terms containing heat capacities.

Equilibria [18] and [19], like [2] through [7] are exchange equilibria between solids. The identical compositions of HB and HS, and of FB and FS, require that two equations be used for each equilibrium. These are

$$[34] \quad \mu_{\underline{HC}} = \mu_{\underline{HD}}$$

and

$$[35] \quad \mu_{\underline{FC}} = \mu_{\underline{FD}}$$

Noting that equation [34] implies

$$[36] \quad \Delta \underline{G}_{\underline{HC}} = \Delta \underline{G}_{\underline{HD}}$$

and combining this with [31] leads to

$$\begin{aligned}
 [37] \quad & \Delta \underline{G}_{\underline{R}}^{\circ} + \Delta \underline{V}_{\underline{R}}^{\circ} (\underline{P} - 1) - \Delta \underline{S}_{\underline{R}}^{\circ} (\underline{T} - 1023) + \int_{1023}^{\underline{T}} \underline{\Delta C}_{\underline{R}} d\underline{T} - \underline{T} \int_{1023}^{\underline{T}} (\underline{\Delta C}_{\underline{R}} / \underline{T}) d\underline{T} \\
 & + \underline{RT} \ln (a_{\underline{HD}} / a_{\underline{HC}}) = 0.
 \end{aligned}$$

Expanding equation [35] gives an equation equivalent to [37], but for the fluoro-endmembers. For both equations the assumption of constant $\Delta \underline{V}$ was made.

In the above general equations both heat capacity and activity are functions of the measurable quantities temperature, pressure, and composition. Before the least squares problem can be solved it is necessary to

adopt functional forms to approximate these quantities. A suitable expression for heat capacity is the function

$$[38] \quad \underline{c} = a + b\underline{T} + c/\underline{T}^2$$

proposed by Maier and Kelley (1932).

The activity term has been treated as outlined by Thompson (1967). Only details specific to this study will be given here. It is interesting to note that although the treatment used here is strictly empirical, the regular symmetric and asymmetric solutions (Thompson, 1967) are identical in functional form to the zeroth order and quasi-chemical approximations of Guggenheim (1952), provided that the substituting atoms or atomic groups are of approximately equal size. Guggenheim's method of development of these mixing models is useful in that it provides the reader with some feeling for the physical significance of the form of the models.

For the solid solution phase C, the relation between composition and activity is given by

$$[39] \quad \underline{x}_{\text{FC}} \frac{RT \ln a_{\text{FC}}}{\text{FC}} + \underline{x}_{\text{HC}} \frac{RT \ln a_{\text{HC}}}{\text{HC}} = \alpha_{\text{FC}} \frac{RT \ln x_{\text{FC}}}{\text{FC}} + \alpha_{\text{HC}} \frac{RT \ln x_{\text{HC}}}{\text{HC}} + \Delta G_{\text{ex,C}}^{1023,1} \\ + \int_1^P \frac{\Delta V_{\text{ex,C}} dP}{1023} - \int_{1023}^T \frac{\Delta S_{\text{ex,C}} dT}{1023} .$$

In the absence of evidence to the contrary, ΔS_{ex} has been assumed to equal zero. (Most of the data presented here are for temperatures near 1023 K and thus give very poor control on ΔS_{ex} .) In addition, ΔV_{ex} is assumed to be constant for each phase. Thus equation [38] reduces to

$$[40] \quad \underline{x}_{\text{FC}} \frac{RT \ln a_{\text{FC}}}{\text{FC}} + \underline{x}_{\text{HC}} \frac{RT \ln a_{\text{HC}}}{\text{HC}} = \alpha_{\text{FC}} \frac{RT \ln x_{\text{FC}}}{\text{FC}} + \alpha_{\text{HC}} \frac{RT \ln x_{\text{HC}}}{\text{HC}} + \Delta G_{\text{ex,C}}^{1023,1} \\ + \Delta V_{\text{ex,C}}^{1023,1} (P - 1) .$$

$\Delta G_{-ex}^{1023,1}$ and $\Delta V_{-ex}^{1023,1}$ remain functions of composition and have been expressed as n^{th} degree polynomials in composition, e.g.

$$[41] \quad \Delta G_{-ex}^{1023,1} = \sum_{i=0}^n a_i x^i.$$

X-ray measurement of the volumes of the solid phases indicates that $\Delta V_{-ex}^{1023,1}$ is zero for all phases except brucite (see Table VI). Even for brucite only the first three terms of the polynomial are necessary to represent the volume function adequately. This leads to

$$[42] \quad \Delta V_{-ex,C}^{1023,1} = x_{FC} x_{HC} \underline{W}_{V,C},$$

where $\underline{W}_{V,C}$ is zero for all phases except brucite.

A fourth degree polynomial was used to approximate $\Delta G_{-ex}^{1023,1}$, although it will be seen later that such a complex function is not necessary for most of the solid solution phases. The result of applying boundary constraints to the polynomial is

$$[43] \quad \Delta G_{-ex,C}^{1023,1} = x_{HC} x_{FC}^2 \underline{W}_{HC} + x_{FC} x_{HC}^2 \underline{W}_{FC} + x_{HC}^2 x_{FC}^2 \underline{E}_C.$$

In equation [43] the \underline{W} 's are equivalent to the \underline{W} 's of Thompson (1967). (\underline{W}_{HC} corresponds to the solution of HC in a crystal of predominantly FC.) \underline{E}_C is the coefficient of the fourth degree term in equation [41]. No theoretical significance has been associated with \underline{E}_C .

From the above it follows that

$$[44] \quad \underline{RT} \ln a_{HC} = \alpha \underline{RT} \ln x_{HC} + x_{FC}^2 \{ \underline{W}_{HC} + 2x_{HC} (\underline{W}_{FC} - \underline{W}_{HC}) - (1 - 4x_{FC} + 3x_{FC}^2) \underline{E}_C + \underline{W}_{V,C} (P - 1) \}$$

and

$$[45] \quad \underline{RT} \ln a_{\underline{FC}} = \alpha \underline{RT} \ln x_{\underline{FC}} + \frac{x_{\underline{FC}}^2}{x_{\underline{HC}}} \{ \underline{W}_{\underline{FC}} + 2x_{\underline{FC}} (\underline{W}_{\underline{HC}} - \underline{W}_{\underline{FC}}) \\ - (1 - 4x_{\underline{HC}} + 3x_{\underline{HC}}^2) \underline{E}_{\underline{C}} + \frac{\underline{W}_{\underline{V,C}}}{\underline{V,C}} (\underline{P} - 1) \} .$$

The equations expressing the equilibria in Table 12 contains a large number of constants (ΔG° 's, ΔS° 's, ΔC 's, \underline{W} 's, etc.), which must be evaluated in order to describe the phase equilibria. In order to reduce the number of variables to be determined on the basis of least squares, those variables not well constrained by the phase equilibrium data and which could be estimated from other sources were evaluated prior to seeking a least squares solution. It is now possible to write equations which express, within the approximations stated, each of the equilibria in Table 12. The equations which follow have been expanded and rearranged so that the parameters to be evaluated all appear in explicit form in the left hand sides of the equations. The exceptions to this are $\Delta S_{\underline{FB}}^\circ$ and $\Delta S_{\underline{HS}}^\circ$. These quantities remain embedded in $\Delta S_{\underline{R}}^\circ$. The data base used to evaluate the right hand sides is given in Table 11. The equations follow. For equilibria [2] through [7],

$$[46] \quad \Delta G_{\underline{HC}}^\circ + \Delta G_{\underline{FD}}^\circ - \Delta G_{\underline{FC}}^\circ - \Delta G_{\underline{HD}}^\circ + (3x_{\underline{FC}}^2 - 2x_{\underline{FC}}) \underline{W}_{\underline{HC}} \\ + (x_{\underline{FC}} - 1)(1 - 3x_{\underline{FC}}) \underline{W}_{\underline{FC}} - (2x_{\underline{FC}} - 6x_{\underline{FC}}^2 + 4x_{\underline{FC}}^3) \underline{E}_{\underline{C}} \\ + (2x_{\underline{FD}} - 3x_{\underline{FD}}^2) \underline{W}_{\underline{HD}} + (1 - x_{\underline{FD}})(1 - 3x_{\underline{FD}}) \underline{W}_{\underline{FD}} \\ + (2x_{\underline{FD}} - 6x_{\underline{FD}}^2 + 4x_{\underline{FD}}^3) \underline{E}_{\underline{D}} = \Delta V_{\underline{R}}^\circ (1 - \underline{P}) + \Delta S_{\underline{R}}^\circ (\underline{T} - 1023) \\ + \alpha \underline{RT} \ln \left\{ \frac{(x_{\underline{FC}} - x_{\underline{FC}} x_{\underline{FD}})}{(x_{\underline{FD}} - x_{\underline{FC}} x_{\underline{FD}})} \right\} \\ + (\underline{P} - 1) \{ (2x_{\underline{FD}} - 1) \underline{W}_{\underline{V,D}} + (1 - 2x_{\underline{FC}}) \underline{W}_{\underline{V,C}} \} .$$

For equilibrium [8],

$$\begin{aligned}
 [47] \quad & \Delta G_{\text{HC}}^{\circ} - \Delta G_{\text{FC}}^{\circ} + (3x_{\text{FC}}^2 - 2x_{\text{FC}})W_{\text{HC}} + (x_{\text{FC}} - 1)(1 - 3x_{\text{FC}})W_{\text{FC}} \\
 & - (2x_{\text{FC}} - 6x_{\text{FC}}^2 + 4x_{\text{FC}}^3)E_{\text{C}} = 2\Delta G_{\text{H}_2\text{O}}^{\circ} - 2\Delta G_{\text{HF}}^{\circ} + \Delta V_{\text{solids,R}}^{\circ}(1 - P) \\
 & + \Delta S_{\text{R}}^{\circ}(T - 1023) + \alpha RT \ln\{x_{\text{FC}}/(1 - x_{\text{FC}})\} + 2RT \ln(f_{\text{H}_2\text{O}}/f_{\text{HF}}) \\
 & + (P - 1)(1 - 2x_{\text{FC}})W_{\text{V,C}}.
 \end{aligned}$$

For equilibria [8] through [16],

$$\begin{aligned}
 [48] \quad & \sum_{\text{C}} \nu_{\text{C}} \Delta G_{\text{C}}^{\circ} + \sum_{\text{C} \neq \text{H}_2\text{O}} [\nu_{\text{C}} x_{\text{FC}}^2 \{(2x_{\text{FC}} - 1)W_{\text{HC}} + 2(1 - x_{\text{FC}})W_{\text{FC}} \\
 & - (1 - 4x_{\text{FC}} + 3x_{\text{FC}}^2)E_{\text{C}}\}] = \Delta V_{\text{solids,R}}^{\circ}(1 - P) + \Delta S_{\text{R}}^{\circ}(T - 1023) \\
 & - \int_{1023}^T \frac{\Delta C_{\text{R}}}{T} dT - T \int_{1023}^T \frac{(\Delta C_{\text{R}}/T)}{T} dT - \nu_{\text{H}_2\text{O}} RT \ln f_{\text{H}_2\text{O}} - \frac{RT}{\sum_{\text{C} \neq \text{H}_2\text{O}} \nu_{\text{C}}} (\alpha \sum_{\text{C}} \nu_{\text{C}} \ln x_{\text{C}}) \\
 & - \sum_{\text{C} \neq \text{H}_2\text{O}} \left\{ \left(\frac{P}{T} - 1 \right) \nu_{\text{C}} x_{\text{FC}}^2 W_{\text{V,C}} \right\},
 \end{aligned}$$

where the ν_{C} are given by equation [28]. Pairs of equations corresponding to equations [34] and [35] of the form of [48] may be used to express equilibria [18] and [19]. It is evident that, provided all fluid species are treated in a manner analogous to that for H_2O and proper ν_{C} are chosen, equation [48] will represent all the equilibria considered in Table 12. The α which appears in some of the above equations is the number of sites per formula unit upon which mixing is occurring. Using the formula units given in Table 2, $\alpha = 2$ for all solid solution phases.

Equations [46], [47], and [48] have been applied to the data listed in Table 7 and to the data of Crane and Ehlers (1969) and Chernosky (1974) listed in Table 13. In order to utilize equilibrium data involving inter-

mediate sellaitite it has been necessary to estimate the compositions of intermediate sellaitite coexisting with periclase, brucite, and sellaitite. This has been done by noting that a bulk composition of MgOHF can be crystallized to 100% intermediate sellaitite while compositions of $\text{Mg}(\text{OH})_{0.9}\text{F}_{1.1}$ and $\text{Mg}(\text{OH})_{1.1}\text{F}_{0.9}$ cannot, and that the cell parameters of intermediate sellaitite (Table IV) indicate very little solid solution. Intermediate sellaitite coexisting with periclase or brucite is estimated to have a composition of $x_{\text{FS}} = 0.49$ while the composition of that coexisting with sellaitite is estimated to be $x_{\text{FS}} = 0.51$. The estimated standard errors assigned to these quantities are 0.02. Since the data of Crane and Ehlers (1969) for coexisting periclase, intermediate sellaitite, sellaitite, and vapor do not include the composition of the sellaitite only equilibrium [14] can be constrained with these data. For this equilibrium, only the data at 1000 bar were used here since these are the only data said by the authors to be reversed.

To further constrain the model, several equations can be written which represent estimates of individual parameters to be evaluated. These equations along with the sources of the data and their estimated standard errors are listed in Table 14.

Appendix 3

Solution of the Least Squares Problem

The system of equations being used to describe the experimental data is highly overdetermined in the sense that there are many more equations than unknowns. Since, as already remarked, the equations involve measured quantities, it may be expected that an exact solution to the equations will not exist. For this reason an approximate solution must be sought. The approximation criterion to be used here is that of least squares.

All the equations to be used to describe this system are linear in the unknowns. The i^{th} equation may be written in the form

$$[52] \quad \sum_{j=1}^{\underline{n}} a_{ij} x_j = b_i .$$

Where the a_{ij} and b_i are constants and the x_j are the unknown parameters, and \underline{n} is the number of unknowns. A system of \underline{m} such equations may be written in the form

$$[53] \quad \underline{A} \underline{x} = \underline{b}$$

where \underline{A} is an \underline{m} by \underline{n} matrix containing the a_{ij} , \underline{b} is a column \underline{m} -vector containing the b_i and \underline{x} is a column \underline{n} -vector containing the x_j . The least squares solution is the \underline{n} -vector \underline{x} for which the euclidean length of the vector $(\underline{A} \underline{x} - \underline{b})$ is a minimum.

If such a solution is found for the set of equations derived directly from the data, no account is taken of the varying degree of certainty to which each of the equations is known. In order to weight the equations according to their uncertainties a weight matrix \underline{L} was applied making the system of equations to be solved

$$[54] \quad \underline{L} \underline{A} \underline{x} = \underline{L} \underline{b} .$$

The matrix \underline{L} was derived from an estimate of the covariance matrix \underline{C}_{eq} of the equations. This was done by computing the Cholesky factorization of \underline{C}_{eq} to produce the lower triangular matrix \underline{F} such that

$$[55] \quad \underline{C}_{eq} = \underline{F} \underline{F}^T .$$

\underline{L} is then defined by the relation

$$[56] \quad \underline{L} = \underline{F}^{-1} .$$

The covariance matrix \underline{C}_{eq} was estimated by the relation

$$[57] \quad c_{\underline{i}\underline{j}} = \sum_k \frac{\partial f_{\underline{i}}}{\partial y_k} \frac{\partial f_{\underline{j}}}{\partial y_k} \sigma_{y_k}^2$$

In the above relation $c_{\underline{i}\underline{j}}$ is the covariance of equations \underline{i} and \underline{j} . The $f_{\underline{i}}$ are defined by the relation

$$[58] \quad f_{\underline{i}} = \left(\sum_j a_{\underline{i}\underline{j}} x_j \right) - b_{\underline{i}}$$

The y_k are the experimentally determined quantities such as mole fraction, temperature, pressure, and volume. The $\sigma_{y_k}^2$ are the variances of the y_k .

In order to simplify calculation of \underline{C}_{eq} the assumption has been made that only errors in the determination of mole fraction, temperature, and in the case of buffered experiments, fluid composition contribute significantly to the covariances. Further, even the errors in temperature measurement were found to be significant only for equilibria involving a fluid phase.

In order to produce a solution vector that would reproduce the data it was also necessary to arbitrarily overweight those equations which describe equilibrium between three solid phases, at least one of which is a solid solution phase, and the vapor. This was done by reducing σ_x for the solid solution phases involved by a factor of five. This has a secondary effect of making it necessary that the covariances be set to zero between these equations and all others correlated to them by virtue of composition measurements.

The least squares solution of equation [53] may be written as

$$[59] \quad \underline{x} = [\underline{GA}]^+ \underline{Gb}$$

where $[\underline{GA}]^+$ is the pseudoinverse of \underline{GA} . The pseudoinverse of a matrix \underline{A}

may be obtained from its singular value decomposition (Golub and Reinsch, 1970; Lawson and Hanson, 1974). The singular value decomposition was accomplished by use of the University of British Columbia Computing Centre subroutine SOLSVD (Streat, 1973). The singular value decomposition yields

$$[60] \quad \underline{A} = \underline{U} \underline{S} \underline{V}^T$$

where if \underline{A} is a m by n matrix, then \underline{U} is an m by m orthogonal matrix, \underline{V} is an n by n orthogonal matrix and \underline{S} is an m by n diagonal matrix. \underline{A}^+ may be defined by the relation

$$[61] \quad \underline{A}^+ = \underline{V} \underline{S}^+ \underline{U}^T$$

where \underline{S}^+ is an n by m diagonal matrix whose diagonal elements s_i^+ are given by

$$[62] \quad s_i^+ = \begin{cases} 1/s_i & \text{for } s_i > 0 \\ 0 & \text{for } s_i = 0 \end{cases}$$

where the s_i are the diagonal elements \underline{S} .

The covariance matrix of the members of the solution vector \underline{x} has been estimated as $\sigma^2 \underline{C}$, where the expression

$$[63] \quad \sigma^2 = \|\underline{Ax} - \underline{b}\|^2 / (m - n)$$

is used to evaluate the scale factor σ^2 and the unscaled covariance matrix \underline{C} is defined by

$$[64] \quad \underline{C} = \underline{V} \underline{S}^+ \underline{S}^+ \underline{V}^T.$$

The correlation matrix may be obtained from the covariance matrix by the relation

$$[65] \quad \rho_{ij} = \sigma_{ij}^2 / \sigma_{ii} \sigma_{jj}$$

where ρ_{ij} is the correlation coefficient and σ_{ij}^2 the covariance for x_i and x_j .

A more detailed account of the computational methods used and several useful fortran codes may be found in Lawson and Hanson (1974). An introduction to least squares problems may be found in Bevington (1969). A more rigorous approach is presented by Plackett (1960).