# Gibbs Energy Minimization in Gas + Liquid + Solid Systems

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**ABSTRACT:** An algorithm is described for the calculation of equilibrium compositions of multiple highly nonideal liquid and solid solutions, as well as pure stoichiometric phases, coexisting with a mixture of ideal gas species at fixed temperature and pressure. The total Gibbs free energy of the system is approximated as a quadratic function of the compositions of the gas phase and stable condensed phases, in an orthogonal basis set of pure elements. Only changes in thermal energy and energy related to pressure-volume work are considered. The total Gibbs energy is minimized directly by use of both the slope and the curvature of the Gibbs energy surface with respect to the gas and condensed phase compositions in the basis elements. The algorithm described has been implemented in a computer code for the calculation of condensation sequences for cosmic nebular gases enriched in dust. Machine, compiler and library requirements for performing these calculations in the C programming language are compared. © 2000 John Wiley & Sons, Inc. J Comput Chem 21: 247–256, 2000

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## Introduction

Calculations of the equilibrium distribution of matter in a system consisting of more than one phase provide the foundation for understanding mass transfer in natural and synthetic chemical systems. This is true even in nonequilibrium processes, such as those limited by diffusion or kinetics, where the driving forces of irreversible processes can frequently be parameterized in terms of departures of systems from thermodynamic equilibrium. Chemical equilibrium calculations have been an important minimization problem since before the advent of the digital computer.[1,2] Previous applications include rocket fuel combustion,[3] condensation of solids in solar nebula gas,[4] and more recent treatments of gas + solid + liquid equilibria in solar gas.[5,6] Progress in this area has increasingly been driven by the recognition that nonideal solid and liquid solutions are important reservoirs of the most abundant elements in natural systems.[7]

The standard technique applied to the condensation problem[5,8–10] uses Lagrange multipliers and first-derivatives of the Gibbs energy, as described amply elsewhere.[1,9] We will describe a quadratic method for finding the minimum in the total Gibbs free energy in systems where matter is distributed among multiple highly nonideal liquid and solid solutions and a vapor composed of a mixture of ideal gas species, all at fixed temperature and pressure. A quadratic approach has not previously been applied to such systems in cosmochemistry, and was adopted to allow the inclusion of solid solution models having components with negative fractional molality, and to incorporate second derivatives of the system Gibbs energy with respect to composition, necessitated by the flatness of the Gibbs energy surface due to the coexistence of multiple solid and/or liquid solutions. The algorithm follows earlier work on chemical mass transfer in magmatic systems, in which equilibria were calculated between nonideal silicate and oxide solid solutions and a 15-component silicate liquid.[7] A program implementing that work[7] was made available to the geological community in the early 1990's, in the form of an executable computer code labeled "MELTS," which has been applied with success to geochemical modeling of the crystallization of dry natural terrestrial silicate liquids,[11,12] particularly at low total pressures, $P^{tot} \leq 10^{10}$ dyne/cm$^2$ (= 10 kbar = 1 GPa).

Models simulating the condensation of gases of solar nebula composition, at $P^{tot} \leq 10^3$ dyne/cm$^2$, have provided fundamental insights into the formation of the earliest solar system materials, the constituents of the chondrite meteorites. Wildt[13] was the first to model condensation in stellar environments. Urey[14] calculated various silicate stability fields for simple cases. Wood[15] derived the pressure-temperature (P-T) stability fields of liquid and solid iron, forsterite ($Mg_2SiO_4$), and enstatite ($MgSiO_3$). Larimer[16] considered equilibrium condensation at $10^6$ and $6.6 \times 10^3$ dyne/cm$^2$. Grossman[4] was the first to include mass-balance constraints in calculating the condensation sequence of a cooling gas of solar composition. Since then, several groups have performed similar calculations for special cases.[5,8,10,17–21] Lodders and Fegley[22] have reviewed the history of condensation calculations for reduced stellar environments.

Previous work on the condensation problem has suffered from one or a combination of deficiencies: neglecting the effect of solid solution of major elements on the stability fields of condensed phases, lack of consideration of nonideal solid solution of major elements in minerals, an inability to correctly treat silicate liquids, or a lack of internal consistency between models for condensed solution phases. Yoneda and Grossman[5] were the first to successfully treat liquids composed of the oxides CaO—MgO—$Al_2O_3$—$SiO_2$; however, the most interesting liquid droplets preserved as glass in the oldest meteorites are chondrules. These glassy beads contain significant dissolved FeO, $TiO_2$, $K_2O$, and $Na_2O$, and usually include crystalline silicate minerals. Many of these minerals within chondrules are solid solution phases, such as olivine (Fe, Mg, Ca)$_2SiO_4$, pyroxene (Ca, Mg, $Fe^{2+}$, $Ti^{4+}$, $Fe^{3+}$, Al)$_2$(Si, Al, $Fe^{3+}$)$_2O_6$, and spinel (Fe, Mg, $Fe^{3+}$, $Cr^{3+}$, Al, $Ti^{4+}$)$_3O_4$. The development of the algorithm discussed here, and its application,[6] resulted from our belief that the origin of chondrules could be understood by incorporating the MELTS liquid model[7] into condensation calculations. The "standard" approach[3] to this problem is well suited to consideration of pure phases, but less effective when complex solid and liquid solutions are present, particularly those with internal ordering of substituents, those modeled using components that may have negative molecular fractions, and those that are highly nonideal.

In the general heterogeneous equilibrium problem, a reservoir of material exists, in the liquid or gaseous state, with which matter in other states reacts, from which matter precipitates or condenses, or into which matter melts, sublimes, or evaporates. For example, in a magmatic system, solid mineral species precipitate from a reservoir of silicate liq-

uid, and the liquid plus solids constitute the system, usually considered closed. In the nebular condensation problem, the gas reservoir, plus the solid and liquid condensates, constitute the system. In both examples, the reservoir contains some amount of every element present in the system, while individual precipitates or condensates contain subsets of the elements. At any particular pressure and temperature at which the system is in thermodynamic equilibrium, there is a unique distribution of matter between the reservoir and the condensates that are thermodynamically stable relative to the reservoir. This equilibrium state is characterized by an extremum in the thermodynamic function of state most convenient to describe the system, here chosen to be the Gibbs free energy. An algorithm for finding this equilibrium, described in numbered sections below, is: (1) solve the speciation of the gas by the BNR technique. (2) Assess the stability of each potential condensate relative to the gas reservoir; add a small amount of the most stable condensate, if any, to the system. (3) Minimize the total thermodynamic potential energy of the system, by redistributing matter among the reservoir and stable condensates; see if any other condensates are stable (2), and, if so, repeat (3); remove any condensates present in vanishingly small amounts, and repeat 1–3; assess chemical potential balance between gas and condensed phases.

Sequences of such calculations can be performed to elucidate the reversible behavior of parcels of matter in response to changes in temperature or pressure; however, we do not address here any of the spatial or temporal aspects of chemical mass transfer. The algorithms presented here have been implemented in a computer program ("VAPORS"), which contains data for 23 elements, distributed among 374 gas species, and a wide variety of potential condensates.[6]

## Model for Vapor Phase (1)

The vapor constitutes the reservoir from which solids and liquids condense. The composition of the vapor, regardless of its speciation, can be described uniquely by any orthogonal (linearly independent) subset of the species present, most conveniently by the basis vector $\mathbf{n}_{\text{gas}}$ corresponding to the number of mol of each element present. We can uniquely determine the speciation of the gas (how much C goes into $C_2H_2$, $CH_4$, $CO_2$, etc.) from the thermodynamic data for the compounds, and thus determine the Gibbs free energy of the vapor for any $T$, $P$, and $\mathbf{n}_{\text{gas}}$.

For every gas species, it is assumed that the ideal gas law holds. This is reasonable at the low pressures ($\leq 10^5$ dyne/cm$^2$, 1 bar = $10^6$ dyne/cm$^2$) of nebular systems. The internal speciation, or homogeneous equilibrium state of the gas at a particular $T$ and $P^{\text{tot}}$, is obtained by writing expressions for the partial pressures of all the species $j$ as functions of the partial pressures of the monatomic species of the basis elements $i$:

$$P_j = K_j \cdot \prod_i^{\text{elements}} P_i^{v_{ij}} \tag{1}$$

where $v_{ij}$ is the stoichiometric coefficient of element $i$ in gas species $j$, $K_j$ is the equilibrium constant for formation of gaseous species $j$ from the monatomic gaseous species at a particular $T$ and $P^{\text{tot}}$, and $K_j$ is written in terms of partial pressures. Mole fractions of species $j$ in the gas are related by an equilibrium constant $K_j^x$:

$$X_j = K_j^x \cdot \prod_i^{\text{elements}} X_i^{v_{ij}},$$

$$\text{through} \quad P_j = \frac{c_j}{C^{\text{tot}}} \cdot P^{\text{tot}} = X_j \cdot P^{\text{tot}} \tag{2}$$

where $c_j$ is the number of mol of species $j$ in the gas phase, and $C^{\text{tot}}$ is the sum of the $c_j$. The different $K$'s are, therefore, related, through stoichiometry of species, by:

$$\log K_j^x = \log K_j + \left( \sum_i^{\text{elements}} v_{ij} - 1 \right) \cdot \log P^{\text{tot}} \tag{3}$$

(the "1" occurs because 1 mol of species $j$ is produced), so species with more atoms are more stable at higher total pressure, following Le Chatelier's principle. For a particular (fixed) composition of the gas, there is one mass balance constraint for the total number of mol $n_i$ of each element $i$ in the gas phase:

$$n_i = \sum_j^{\text{species}} v_{ij} c_j \tag{4}$$

which can, of course [through eq. (2)], be written in terms of the $K_j^x$, enabling construction of a system of equations suitable for determination of the partial pressures of the basis elements, given $P^{\text{tot}}$, $T$, and the bulk composition vector $\mathbf{n}_{\text{gas}}$. This system of equations has a unique solution for every bulk composition of the gas. That is, no possibility exists for the coexistence, at an equilibrium state, of two immiscible gas phases.

We determine the speciation of the vapor using a BNR (Brinkley-NASA-RAND) numerical technique

(reviewed in ref. 1, following ref. 3, cf. ref. 2). In this method the equilibrium conditions (2) are held rigorously, and the deviation of the mass balance eq. (4) from equality is minimized. That is, convergence is defined such that

$$\left| n_i - \sum_{j}^{\text{species}} v_{ij} c_j \right| \leq \varepsilon_g \qquad (5)$$

for all the elements $i$, where $\varepsilon_g$ is set to $10\tau$, where $\tau$ is the machine precision, of order $10^{-31}$ in our calculations. Note that we apply eqs. (1) to (4) only to the gas reservoir, not to condensing species. Unlike the "standard" technique,[3] the calculations described here treat the gas as a distinct phase, and are performed in modules separate from the very different procedure used to minimize the Gibbs energy of the entire system, described below.

## Assessing Stability of Condensed Phases (2)

The vapor is allowed to simultaneously condense one of two liquid solutions, and an unlimited number of pure stoichiometric solids and complex solid solution phases. We have implemented Berman's[23] model characterizing CaO—MgO—$Al_2O_3$—$SiO_2$ (CMAS) liquids using a 12-parameter, fourth-degree Margules-type function to describe deviations of thermodynamic mixing functions from ideality. This model has been used with some success to describe stable and metastable liquid immiscibility, and liquidus phase relations, in the CMAS system.[24] Also present is a $SiO_2$—$TiO_2$—$Al_2O_3$—$Fe_2O_3$—$Fe_2SiO_4$—$Mg_2SiO_4$—$MgCr_2O_4$—$CaSiO_3$—$Na_2SiO_3$—$KAlSiO_4$—$Ca_3(PO_4)_2$—$H_2O$ liquid, which is a subset of the 15-component silicate liquid described by Ghiorso and Sack[7, 25] using a symmetric regular solution model. Multicomponent solid solution models for olivine[26] (Fe, Mg, Ca)$_2SiO_4$, spinel[27, 28] (Fe, Mg, $Fe^{3+}$, $Cr^{3+}$, Al, $Ti^{4+}$)$_3O_4$, pyroxene[26, 29–31] (Na, Ca, Mg, $Fe^{2+}$, $Ti^{4+}$, $Fe^{3+}$, Al)$_2$(Si, Al, $Fe^{3+}$)$_2O_6$, feldspar[32] (KSi, NaSi, CaAl)$AlSi_2O_8$, melilite[33] $Ca_2$(MgSi, $Al_2$)$SiO_7$, and rhombohedral oxides[34] ($Fe_2^{3+}$, $Fe^{2+}$Ti, MgTi, MnTi)$O_3$ have been intercorrelated, and the 15-component silicate liquid model of ref. 7 has been calibrated against a very large database of crystal–liquid equilibria using the descriptions of these solid solutions, all based on the comprehensive thermodynamic database of Berman[35] for end-member (pure stoichiometric) phases. An asymmetric binary solution model for Fe-Ni-Si-Cr-Co solid alloy is also included, calibrated using published data,[36–38] following Grossman et al.[39] Further information on species and data sources is listed in ref. 6.

Equilibrium expressions for condensation are written in terms of the basis composition variables of the gas, here the monatomic gaseous elements. For example, the condensation of aluminum oxide (corundum) proceeds according to the reaction:

$$2\text{Al}_{\text{gas}} + 3\text{O}_{\text{gas}} = \text{Al}_2\text{O}_{3(\text{solid corundum})}. \qquad (6)$$

Denoting the Gibbs free energy of formation of corundum from the monatomic gaseous elements at a particular temperature and $P^{\text{tot}}$ by $G_{\text{T}}^{\text{cor}}$, corundum is stable relative to the gas, if

$$G_T^{\text{cor}} = -RT \cdot \ln\left[K_{\text{T}}^{\text{cor}}\right] = -RT \cdot \ln\left[\prod_{i}^{\text{elements}} P_i^{v_{ij}}\right]$$
$$= -RT \cdot \ln\left[P_{\text{Al}}^2 \cdot P_{\text{O}}^3\right] \leq 0. \qquad (7)$$

The initial stability of the solids (or liquids) at fixed $P^{\text{tot}}$ and temperature is determined by reference to such equations after solving the gas phase speciation to determine the partial pressures of the monatomic gas species, which are equivalent to their activities at low $P^{\text{tot}}$. The algorithm described by Ghiorso[40] is used for the more complex cases of highly nonideal solid and liquid solutions, where mixing properties of molecular end members in solution must be accounted for in equations analogous to (7). This technique finds the most stable initial solution composition, by matching component activities to corresponding properties of the gas reservoir. Once a phase is determined to be thermodynamically stable relative to the gas, its initial composition is added to the stable condensate assemblage in some initial "seed" quantity (e.g., $10^{-7}\times$ the total mol of elements in the system), which is subtracted from the bulk composition of the gas. At this point, the entire system must be adjusted, in terms of the compositions of gas and condensates, to minimize the thermodynamic potential energy (Gibbs free energy) of the system. By initializing with the most stable initial solution composition relative to the gas reservoir, evolution toward the global minimum Gibbs energy of the solution phase, relative to other phases, is strongly favored, at temperatures well above miscibility gaps in the solid solution phases.

## Minimization of System Thermodynamic Potential (3)

For each phase $p$, there is a vector of orthogonal composition variables $\mathbf{n}_p$, which is the basis set

of thermodynamic components spanning the possible chemical variability of that phase. For example olivine, (Fe, Ca, Mg)$_2$SiO$_4$, is given components Mg$_2$SiO$_4$, Fe$_2$SiO$_4$, and CaMgSiO$_4$, whereas corundum, Al$_2$O$_3$, is treated as a pure, one-component phase. Many phases require calculation of ordering of atoms on sites, or consideration of polymorphic phase transitions to establish their minimum chemical potential energy. These internal, or homogeneous, equilibrium considerations are treated separately for the condensed phases, as they are for the gas, and are thus "transparent" to the system minimization algorithm, as is the speciation of the gas. However determined, there exists a scalar Gibbs energy $G_p$ associated with each phase $p$, such that we can write the chemical potentials of the thermodynamic components of $p$ as the vector $\mathbf{u}_p = (\partial G_p/\partial \mathbf{n})_{T,P}$. The Gibbs energy of a system containing gas plus $m$ condensed phases is just the sum over all the phases: $G = G_{\text{gas}} + G_1 + \cdots + G_m$. The distribution of matter in a system containing a gas phase and $m$ condensed phases may be described in terms of $n$ system components by a column vector $\mathbf{n} = [\mathbf{n}_{\text{gas}}\ \mathbf{n}_1\ \mathbf{n}_2\ \ldots\ \mathbf{n}_m]^{\mathrm{T}}$, the system component vector, composed of the stacked component vectors of the separate phases.

To describe the constraints imposed on the entire system by mass balance, the bulk composition of the entire system is written as a vector $\mathbf{b}$, of length $s$. It is desirable to choose as these $s$ bulk components the same 23 elements that are used to describe the gas phase, because we will wish to transfer matter between gas and condensates as individual atoms, rather than as compounds (e.g., oxides). A matrix $\mathbf{C}$ is then readily constructed, which relates the vector $\mathbf{n}$ to the bulk component vector $\mathbf{b}$, such that $\mathbf{b} = \mathbf{Cn}$. This equation describes the bulk composition constraint on the system.

We can now state succinctly the problem of minimizing the system thermodynamic potential, $G$, with respect to the system components $\mathbf{n}$, subject to the mass balance constraint $\mathbf{b} = \mathbf{Cn}$. Ghiorso[41] has reviewed previous approaches to this problem in the earth sciences and chemical engineering. We start by simplifying the problem using the method described by Ghiorso.[41] Treating all the $n$ system components as independent variables, we can write the chemical potentials, $\mathbf{u} = [\mathbf{u}_{\text{gas}}\ \mathbf{u}_1\ \mathbf{u}_2\ \ldots\ \mathbf{u}_m]^{\mathrm{T}} = (\partial G/\partial \mathbf{n})_{T,P}$. We will also require the second derivatives of $G$ with respect to $\mathbf{n}$, for the entire system, which are elements of the Hessian matrix $\mathbf{H} \equiv (\partial \mathbf{u}/\partial \mathbf{n})_{T,P}$. Matrix $\mathbf{H}$ is block diagonal $n$ by $n$, with blocks corresponding to matrices $\mathbf{H}_{\text{gas}} = (\partial \mathbf{u}_{\text{gas}}/\partial \mathbf{n}_{\text{gas}})_{T,P}$, followed diagonally by a similar matrix for each one of the condensed phases. Calculation of $\mathbf{u}_{\text{gas}}$ and $\mathbf{H}_{\text{gas}}$ are described in section 4, below. Suppose we have some initial guess, $\mathbf{q}$, for the solution to the minimization problem. Use of the second derivatives allows us to approximate the Gibbs energy of the system, using a second-degree Taylor expansion in the $n$ system components, at some point $\mathbf{n}$ near the initial point $\mathbf{q}$:

$$G = G|_{\mathbf{q}} + \mathbf{u}^{\mathrm{T}}|_{\mathbf{q}}(\mathbf{n}-\mathbf{q}) + \tfrac{1}{2}(\mathbf{n}-\mathbf{q})^{\mathrm{T}}\mathbf{H}|_{\mathbf{q}}(\mathbf{n}-\mathbf{q}) + \text{higher order terms} \quad (8)$$

where $|_{\mathbf{q}}$ signifies evaluation of the term to the left at $\mathbf{q}$. If $\mathbf{n}$ is very close to $\mathbf{q}$, such that $(\mathbf{n}-\mathbf{q})^{\mathrm{T}}(\mathbf{n}-\mathbf{q}) \approx 0$, then the higher order terms can be ignored. This approximation for $G$ simplifies the minimization problem considerably.

Solution of what is now a constrained *quadratic* minimization problem can be accomplished using the algorithm provided by Betts,[42] which we summarize briefly here. The bulk composition constraint relates the elements of $\mathbf{n}$ such that there are only $n - s$ independent variables required to uniquely define $\mathbf{n}$. We can determine an $n$ by $n$ orthogonal "projection matrix" $\mathbf{K}$, such that $\mathbf{CK} = \mathbf{R}$, which projects $\mathbf{C}$, $s$ by $n$, into a new matrix $\mathbf{R}$, $s$ by $n$, in which the upper left $s$ by $s$ elements constitute a nonsingular submatrix $\mathbf{R}_1$, and the remaining elements of $\mathbf{R}$ are zero. Then, using $\mathbf{b} = \mathbf{Cn}$, we can write $\mathbf{RK}^{\mathrm{T}}\mathbf{n} = \mathbf{b}$, because $\mathbf{K}$ is orthogonal, and partition $\mathbf{K}^{\mathrm{T}}$ so $\mathbf{K}^{\mathrm{T}} = [\mathbf{K}_1 : \mathbf{K}_2]^{\mathrm{T}}$, where $\mathbf{K}_1$ is $n$ by $s$, and $\mathbf{K}_2$ is $n$ by $(n-s)$. Then we can write $\mathbf{n} = \mathbf{K}_1\mathbf{n}_1 + \mathbf{K}_2\mathbf{n}_2$, where $\mathbf{n}_1$ has length $s$, and $\mathbf{n}_2$ has length $(n-s)$, and compute $\mathbf{n}_1$ using $\mathbf{R}_1\mathbf{K}_1^{\mathrm{T}}\mathbf{n} = \mathbf{b}$, leaving the $\mathbf{n}_2$ still to be determined. To minimize

$$G = G|_{\mathbf{q}} + \mathbf{u}^{\mathrm{T}}|_{\mathbf{q}}(\mathbf{K}_1\mathbf{n}_1 + \mathbf{K}_2\mathbf{n}_2 - \mathbf{q}) + \tfrac{1}{2}(\mathbf{K}_1\mathbf{n}_1 + \mathbf{K}_2\mathbf{n}_2 - \mathbf{q})^{\mathrm{T}}\mathbf{H}|_{\mathbf{q}}(\mathbf{K}_1\mathbf{n}_1 + \mathbf{K}_2\mathbf{n}_2 - \mathbf{q}) \quad (9)$$

with respect to $\mathbf{n}_2$, we set the derivative equal to zero and obtain

$$\mathbf{K}_2^{\mathrm{T}}\mathbf{H}|_{\mathbf{q}}\mathbf{K}_2\mathbf{n}_2 + \mathbf{K}_2^{\mathrm{T}}\mathbf{u}|_{\mathbf{q}} + \mathbf{K}_2^{\mathrm{T}}\mathbf{H}|_{\mathbf{q}}\mathbf{K}_1\mathbf{n}_1 = 0 \quad (10)$$

which is a linear system of equations in $(n - s)$ unknowns, because only the first term on the left is unknown. This is solved for $\mathbf{n}_2$, which with $\mathbf{n}_1$ gives $\mathbf{n}$. Once the vector $\mathbf{n}$ has been determined in this way, we know the direction in which to redistribute matter among the gas and condensate phases to approach the minimum in $G$, but not the magnitude of the redistribution. To avoid moving into potentially infeasible regions of composition space, a new solution $\mathbf{q}' \equiv \mathbf{q} + \alpha(\mathbf{n} - \mathbf{q})$ is chosen, where $\alpha$ is a step length along $\mathbf{n}$, chosen such that $dG(\mathbf{q}')/d\alpha = 0$, and such that $\mathbf{q}'$ does not violate

feasibility tests on the compositions of the condensates present in the system. The new solution $\mathbf{q}'$ describes the distribution of atoms between phases, corresponding to the minimum thermodynamic potential energy of the system, from the point of view of the previous solution. Approximated at $\mathbf{q}'$, however, the derivatives in [eqs. (8)–(10)] will have new values, so $\mathbf{q}'$ becomes the initial guess for obtaining a new solution. Whether the new system component vector corresponds to the minimum chemical potential energy of the system is decided by whether a rearrangement of matter among the system components can be found, which further reduces the system's chemical potential energy. Therefore, we define convergence to a minimum as the lack of significant change ($<10^{-12}$) in the Euclidean norm of the vector $\mathbf{n}$ over two attempts to find a better minimum.

Once convergence is achieved, the system is tested for disappearance or saturation of condensed phases. If the amount of any phase becomes lower than some threshold value (chosen to be $10^{-10}$ mol per mol of atoms in the system, which is $\sim 10^{-3}$ the amount ever found to be stable, regardless of the threshold chosen in extensive testing, and following ref. 10), then that condensate is dropped from the stable assemblage, and the material in it is returned to the gas phase. We also check the new solution again, as described earlier, to determine whether the reservoir is saturated with respect to any other potential condensate phase. If any phase is dropped or added, the minimization must be repeated with the new assemblage of stable condensates. Otherwise, the equilibrium state of the system has been determined for the current $P^{tot}$, temperature, and bulk system composition. Extensive, detailed comparisons were made between results obtained using this algorithm and results of Yoneda and Grossman,[5] who used a standard BNR technique, modified to handle simple nonideal solutions. When identical data were used in both calculations, results were identical to within $\sim 10^{-14}$. Yoneda and Grossman,[5] in turn, carried out extensive comparisons with earlier results (e.g., ref. 4).

Although results obtained by this method in cosmochemical applications are consistent with previous work, multiple nonideal solid and liquid solutions have never been addressed in this way in the cosmochemical literature, and one might ask whether the algorithm attains the global minimum in such systems. One condition for local minima in the total system is the existence of local minima in one or more of the models for specific phases: gas, liquid, or solid(s). That is, the model for one or more phases must be capable of producing immiscibility. We use the same kind of algorithm for the gas phase as have previous workers, and because the gas is a mixture of ideal gas species, multiple minima for the gas do not occur, as implicit in previous work. The CMAS liquid is known to have local minima (immiscibility) in certain regions of its composition space, but these occur well below the temperatures of our calculations, in $SiO_2$-rich compositions.[24] However, it is conceivable that for some combination of parameters, we could compute the (meta)stability of a CMAS liquid which should unmix, and could, therefore, underestimate the stability of liquid. Yoneda and Grossman,[5] using different algorithms but the same liquid model, reported no such unmixing, and we match their results wherever tested, including CMAS–liquid-bearing systems. The formulation of the MELTS liquid model is such that saddle points exist on its Gibbs energy surface, but not local minima, as discussed by Ghiorso et al.[25] The solid solution models we use (e.g., spinel, olivine, pyroxene) produce miscibility gaps that closely match those found in nature and the laboratory, but all the calculations we perform are at temperatures well above known miscibility gaps in the systems of interest. Extensive testing with phases added or removed, and from different initial states, has shown no instances where this algorithm produced false minima in systems such as those illustrated in Figure 1.

## Derivatives of $G$ for the Gas Phase (4)

The numerical algorithms for the complete system require calculation of the change in the thermodynamic potential $G_p$ of every stable phase $p$ in the system, with respect to all possible changes in the composition of that phase, and also calculation of the second derivatives of each $G_p$ with composition. These calculations are performed separately for each phase, depending on the form of the model used to describe its thermodynamic properties. This is rapidly accomplished with a closed form for $(G\mathbf{n}_k)$ for any particular pure phase $k$, but the calculation of these derivatives is slower for phases such as pyroxene[26, 29–31] and spinel,[27, 28] which involve internal ordering of atoms on crystal lattice sites. For any particular composition of such solid solutions, the ordering state must be obtained by iterative solution of statements of homogeneous equilibrium. Determining the sensitivity of the gas phase to small changes in composition requires the most numerical labor at this step.

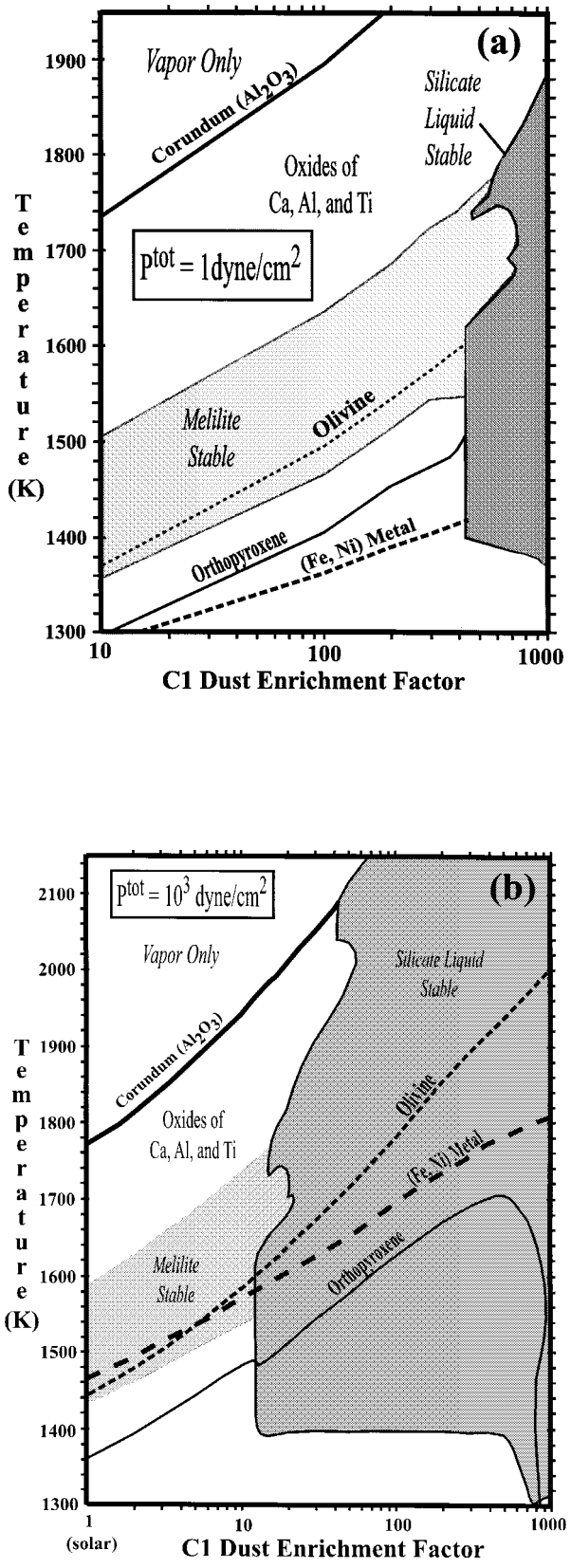


**FIGURE 1.** Stability fields of selected phases in dust-enriched systems.

Because we are removing elements (e.g., Al and O) from the gas to form solids (e.g., $Al_2O_3$), the derivatives $\mathbf{u}_{gas}$ and $\mathbf{H}_{gas}$ must be taken with respect to the total mol of those elements in the gas, not simply with respect to the number of mol of their monatomic gaseous species. Any change in the bulk composition of the gas, $\mathbf{n}_{gas}$, described by the 23 basis elements, will affect mass distribution among all of its 374 chemical species, and therefore, effect a change in the Gibbs energy of the gas. However, there is no analytical solution to the speciation of the gas. We have devised a numerical method to approximate the derivative properties of the gas, and the method works well for the conditions investigated to this point.[6, 21] Up to $(3 \times 23 + 2 \times 23^2)$ calculations of speciation in the gas are required in any particular iteration; however, this can be reduced, because only the derivatives with respect to elements actually condensing in solids or liquids are required. Nevertheless, this is a time-consuming problem.

We start at a particular gas composition $n_0$ for which we have calculated $G_0^{gas}$, and determine $\Delta G^{gas}$ along chords to the surface $G(\mathbf{n}_{gas})$, as follows. We vary $n_i$ sequentially for each element $i$ for which evaluation of $(\partial G/\partial n_i)_{n_{k\neq i}}$, is required, leaving the other elements as at $\boldsymbol{n}_0$, by designating a new composition $\boldsymbol{n}_i^+$ where only element $i$ has been changed from $\boldsymbol{n}_0$, to $n_i = n_i^0 + \varepsilon_i$, and a new composition $\boldsymbol{n}_i^-$ where $n_i = n_i^0 - \varepsilon_i$. We calculate $G^{gas}$ at $\boldsymbol{n}_i^+$ and $\boldsymbol{n}_i^-$ to obtain $G^{i+}$ and $G^{i-}$, respectively. We must increase $\varepsilon_i$ until it attains the smallest value for which $|G^{i+} - G^{i-}| > 100\tau$, where $\tau$ is machine precision, to obtain an adequate, nonzero, approximation to $(\partial G/\partial n_i)_{n_{k\neq i}}$, at $\boldsymbol{n}_0$. To obtain the Hessian matrix $(\partial^2 G/\partial n_i \partial n_j)_{n_{k\neq i,j}}$ for pairs of basis elements $i$ and $j$, we vary $n_j$ as we did $n_i$, about the previously defined compositions $\boldsymbol{n}_i^+$ and $\boldsymbol{n}_i^-$, obtaining a total of four gas compositions, $\boldsymbol{n}_{ij}^{++}$, $\boldsymbol{n}_{ij}^{+-}$, and $\boldsymbol{n}_{ij}^{-+}$, $\boldsymbol{n}_{ij}^{--}$, which surround $\boldsymbol{n}_0$ in the composition dimensions $i$ and $j$. As for $\varepsilon_i$, the variation $\varepsilon_j$ must be sufficiently large than $|G(\boldsymbol{n}_{ij}^{++}) - G(\boldsymbol{n}_{ij}^{+-})| > 100\tau$ and $|G(\boldsymbol{n}_{ij}^{-+}) - G(\boldsymbol{n}_{ij}^{--})| > 100\tau$. These quantities yield $(\partial G^{i+}/\partial n_j)_{n_{k\neq j}}$ and $(\partial G^{i-}/\partial n_j)_{n_{k\neq j}}$, which in turn, yield $(\partial^2 G/\partial n_i \partial n_j)_{n_{k\neq i,j}} \sim [(\partial G^{i+}/\partial n_j)_{n_{k\neq j}} - (\partial G^{i-}/\partial n_j)_{n_{k\neq j}}]/dn_i$.

In addressing condensation in solar gases, the initial relative mol numbers of constituent elements vary by seven orders of magnitude over the 23 most abundant elements. This poses numerical problems in the minimization of the thermodynamic potential for complex systems of gas + solids + liquids. With the great mass of gas consisting of volatile species

containing H, He, C, O, and N, the thermodynamic potential of the gas becomes relatively insensitive to the decreasing amounts of refractory elements such as Al, Ca, and Ti, which remain in the gas as it cools, but it is the behavior of these rock-forming elements, which is of greatest interest! One way to assess how closely the system has converged to its minimum is to calculate the deviation from chemical potential balance of the formation reactions of each of the stable condensates [e.g., eq. (6)]. The ability of the algorithm to minimize these deviations is a function of the ability to calculate $\mathbf{u}_{\text{gas}}$ and $\mathbf{H}_{\text{gas}}$ by the method outlined above, hence, of machine precision ($\tau$). At low temperatures, when some elements are depleted to vanishingly small abundances in the gas phase, these deviations become large, and the calculation is halted. It is a general failing of all algorithms of this type (e.g., ref. 7), that all the basis components of the system (e.g., elements, or oxides) must be present in some nonzero amount in the phase, which constitutes the reservoir, at all steps of the calculation.

### INITIAL STATE

If the calculation is begun at a temperature and pressure where there are multiple stable condensed phases, particularly solid or liquid solutions, then the algorithm takes a great deal of time to determine the identities of these phases, given no other initial information. We, therefore, routinely begin calculations at temperatures sufficiently high that few or no condensed phases are stable, and iterate to successively lower temperatures, for a fixed $P^{\text{tot}}$ and system bulk composition, using the solution at the previous temperature step as the initial state. Generally, the result for a particular $P^{\text{tot}}$, temperature, and bulk composition can be used as the initial state for calculation at a similar set of conditions. Regardless of the method used to establish the initial state of the system, the same result is obtained from the calculation. The algorithm is in no way optimized for any particular (e.g., $H_2$-rich) bulk composition of the system.

## Machine and Compiler Considerations

The numerical algorithms require calculations of the gradient ($\mathbf{u}_p$) and Hessian ($\mathbf{H}_p$) of the thermodynamic potential $G_p$ of every phase $p$ in the system, with respect to all possible change in its composition $\mathbf{n}_p$. As described above, the methods for approximating these quantities for the gas are sensitive to numerical precision. At IEEE double (64-bit) precision, the program fails when the mol fractions of refractory elements remaining in the gas become moderately small (order $10^{-13}$). At IEEE quadruple (long double, 128-bit) precision, this limit is decreased by ~10 orders of magnitude, sufficient for the success of the calculations described in ref. 6. In all cases examined in detail, breakdown of the algorithm is signalled by its inability to discern the gradient in system composition that points toward the true minimum, resulting in extremely small changes leading nowhere useful.

Because full quadruple precision (128-bit, or 32 significant digits) is required of the algorithm, the computation can only be accomplished in reasonable time on "big endian" processors. We use the C programming language, for which the quadruple precision floating point libraries for the IRIX and SunPro C++ compilers seem to be particularly efficient. We obtained ~2.8× faster results on an SGI Origin 2000 with R10000 (180 MHz) cpus running IRIX 6.4 and the MIPSPro C compiler, in benchmarks on nearly identical code compiled and run on a Sun Ultra Enterprise 4000 with UltraSparc III cpus (248 MHz), running Solaris 2.5.1 with the SunPro v. 4.0 C compiler, in January of 1998. This is noted to emphasize the sensitivity of these calculations to the libraries upon which they call, not to endorse any particular operating system, and may reflect, in part, our own inability to optimally "tweak" each configuration. Even in the SGI environment, the calculations proceed slowly. On the R10000 processor, 2 weeks were required to calculate the condensation history of a solar gas enriched 1000 times by a dust of carbonaceous chondrite composition[6] from 2400 to 1300 K in 10° steps. As noted above, most of this time is spent solving speciation in the gas for variations in its composition, necessary to set up the system minimization matrices. This speed is running "flat out," with minimum file output between temperature steps, no swapping to disk, and no interactive or console input/output. Although the algorithm is cpu-intensive, it is relatively compact, requiring 10–15 MB of random access memory throughout the run, depending on the number of condensed phases. The availability of RAM, or the need to swap to disk memory, is not a factor in any of the speed tests described above. It would be optimal to use fast, arbitrarily precise floating point routines in the most sensitive parts of the calculation, but this goal has proven elusive. The algorithm would also be highly amenable to parallelization.

## Results

The chondritic meteorites contain spherules thought to be quenched silicate liquid droplets, FeO-rich olivines, and other objects of enigmatic origin, but thought to result from condensation of a hot gas prior to planet formation. To investigate the possible relationship between condensation processes and the origin of the constituents of chondrites, the above technique was developed to treat systems where $P^{tot}$ is high enough, or which are rich enough in condensable elements, that multiple complex solid and liquid solution phases condense. In the gas, the condensable, rock-forming elements are present in trace amounts, diluted by enormous concentrations of H and He.[6] Because most of the condensable fraction of solar system matter may have entered the presolar nebula in the form of interstellar dust, it is reasonable to consider that the central regions of the protoplanetary solar disk were enriched, relative to the gas, in dust having the composition of C1 chondrites, whose composition is representative of the condensable fraction of solar system matter. After those regions are totally vaporized, such enrichment increases the effective oxygen fugacity of the resulting gas, relative to a gas of solar composition, and promotes the formation of condensates at temperatures where they are partially or fully molten. Detailed results of calculations at several combinations of dust enrichment factor and $P^{tot}$ have been presented elsewhere,[6] but Figure 1 shows phase relationships over a wide range of dust enrichments, at $P^{tot}$ bracketing those thought to obtain in the inner part of the protoplanetary disk.

The fields for oxides of Ca, Al, and Ti, and for solid melilite, are thought to be those in which refractory inclusions in meteorites form.[5] Together, olivine $(Mg, Fe, Ca)_2SiO_4$, orthopyroxene $(Mg, Fe)SiO_3$, and metal alloy (Fe, Ni, Co, Cr, Si) solutions dominate the mineralogy of chondritic meteorites, and account for the bulk of the condensable fraction of solar system matter. The stability field of silicate liquid becomes more extensive with increasing $P^{tot}$ and, at any given $P^{tot}$, widens with increasing dust enrichment. For any particular system bulk composition, the condensed solid assemblage, and/or liquid, are rich in CaO, $Al_2O_3$, and $TiO_2$ at high temperature, but increase their MgO and $SiO_2$ contents, relative to CaO, $Al_2O_3$, and $TiO_2$, as the temperature falls. At high dust enrichments, significant amounts of Fe, Na, and K condense as oxide components in both solid and liquid silicates at temperatures above 1400 K. It is increasingly clear that the understanding of condensed matter in the early solar system will depend upon development of better data and models for liquid and solid solutions, which will, in turn, require more sophisticated computational techniques.

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