SOLID-SOLUTION AQUEOUS-SOLUTION EQUILIBRIA: THERMODYNAMIC THEORY AND REPRESENTATION

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ABSTRACT. Thorstenson and Plummer's (1977) "stoichiometric saturation" model is reviewed, and a general relation between stoichiometric saturation K_{ss} constants and excess free energies of mixing is derived for a binary solid-solution $B_{1-x}C_xA$:

$$G^E = RT[\ln K_{ss} - x\ln(xK_{CA}) - (1 - x)\ln((1 - x)K_{BA})]$$

This equation allows a suitable excess free energy function, such as Guggenheim's (1937) sub-regular function, to be fitted from experimentally determined K_{ss} constants. Solid-phase free energies and component activity-coefficients can then be determined from one or two fitted parameters and from the endmember solubility products K_{BA} and K_{CA}. A general form of Lippmann's (1977, 1980) "solutus" equation is derived from an examination of Lippmann's (1977, 1980) "total solubility product" model. Lippmann's $\Sigma\Pi$ or "total solubility product" variable is used to represent graphically not only thermodynamic equilibrium states and primary saturation states but also stoichiometric saturation and pure phase saturation states.

Experimental evidence indicates that while stoichiometric saturation states may under certain conditions be attained during the dissolution of relatively insoluble solids (such as Mg-calcites and Sr-aragonites), thermodynamic equilibrium can nevertheless be approached for more soluble solid-solutions, such as the alkali halides.

INTRODUCTION

Solid-Solution Aqueous-Solution ("SSAS") processes are of considerable importance to the study of rock-water interactions (McIntyre, 1963; Saxena, 1973; Braitsch, 1971). Natural minerals, and in particular iron and manganese oxy-hydroxides, clay minerals, carbonates, sulfates and evaporite minerals, always contain a certain proportion of impurities in solid-solution (Palache, Berman, and Frondel, 1951; Deer, Howie, and Zussmann, 1963). Understanding SSAS processes, that is, understanding the role of impurities in mineral-aqueous-solution interactions, is of fundamental importance to geochemical studies.

The study of SSAS thermodynamics was initiated around the turn of the century (Berthelot, 1872; Nernst, 1891; Henderson and Kracek, 1927; Doerner and Hoskins, 1925) mainly as a result of the need for high-purity chemical reagents. Of main concern were the laws governing the entrainment of impurities during precipitation processes. Distribution coefficients were used to express the partitioning of an

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impurity ion C^+ between an aqueous-solution and a solid phase $B_{1-x}C_xA$:

$$D = \frac{\chi_{CA}}{\chi_{BA}} \Bigg/ \frac{[C^+]}{[B^+]} \tag{1}$$

where χ_{BA} and χ_{CA} are the solid-phase mole fractions of components BA and CA: $[B^+]$ and $[C^+]$ are the aqueous activities of B^+ and C^+.

While distribution coefficients can be used as a measure of thermodynamic equilibrium in SSAS systems, they do not directly provide a measure of the solubility of a solid-solution. Distribution coefficients are theoretically derived from the two basic conditions defining thermodynamic equilibrium in a binary SSAS system $BA-CA-H_2O$:

$$[B^+][A^-] = K_{BA}a_{BA} = K_{BA}\chi_{BA}\gamma_{BA} \tag{2}$$

$$[C^+][A^-] = K_{CA}a_{CA} = K_{CA}\chi_{CA}\gamma_{CA} \tag{3}$$

where $[A^-]$ is the activity of A^- in the aqueous solution, K_{BA} and K_{CA} are the pure endmember solubility products, a_{BA} and a_{CA} are the solid-phase activities of BA and CA, and γ_{BA} and γ_{CA} are the solid-phase activity coefficients.

In dividing eqs (2) and (3) one by another, as is implicitly done in deriving the distribution coefficient expression (eq 1), information about the aqueous concentration or activity of the non-substituting ion A^- and therefore about the solubility of the solid-solution is lost. To overcome this problem, geochemists[1] have often expressed the solubility of a solid-solution $B_{1-x}C_xA$ as follows:

$$IAP_{ss} = [C^+]^x[B^+]^{1-x}[A^-] = K_{ss} \tag{4}$$

where IAP_{ss} is the observed ion activity product, and K_{ss} is the applicable solubility constant at a given temperature and pressure, for a given solid-solution composition $B_{1-x}C_xA$. In 1977, Thorstenson and Plummer presented a theoretical framework for this formulation, giving the name "stoichiometric saturation" to the state represented by the constant K_{ss} and showing how thermodynamic equilibrium could be predicted from experimental measurements of stoichiometric saturation.

Lafon (1978) criticized the concept of stoichiometric saturation as well as Thorstenson and Plummer's laboratory approach in determining K_{ss} constants. His arguments centered mainly around the applicability of stoichiometric saturation to natural systems and especially to precipitation processes. Nevertheless, the basic validity of the K_{ss} expression as an equilibrium constant following the law of mass action was not put into question until Lippmann (1977, 1980, 1982a, b), who objected to the K_{ss}

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[1]For example, Garrels and Christ (1965), Berner (1975), Kittrick (1973), Denis (1982), Denis and Michard (1983), Walter and Morse (1984), Michard (1986).

formulation and suggested a different equilibrium variable, which he called $\Sigma\Pi$ or the "total solubility product":

$$\Sigma\Pi = |A^-|(|B^+| + |C^+|) = K_{BA}a_{BA} + K_{CA}a_{CA} \qquad (5)$$

where a_{BA} and a_{CA} are the solid-phase activities of components BA and CA.

The primary objective of this paper is to compare the equilibrium expressions proposed by the Thorstenson and Plummer and Lippmann models, evaluating the conditions for which these models may be individually appropriate and determining which of their components, if any, should or could be used in a comprehensive theory of SSAS thermodynamics. The fundamental principles and assumptions built into the two models will be reviewed. Experimental evidence in support of both the Thorstenson and Plummer and Lippmann models will be presented, so that relations between the two models may be better understood. Conventional pure phase solubility-product theory will also be discussed and compared to solid-solution solubility theory, in an effort to determine conditions and processes for which SSAS theory may be indispensable.

LIST OF SYMBOLS

a_0, a_1	First two dimensionless coefficients in the Redlich and Kister and Guggenheim expressions for solid-phase activity coefficients and excess free energy (eq 35).
$|A^-|, |B^+|, |C^+|$	Activities of A^-, B^+, and C^+ ions in the aqueous phase (eqs 1, 2, 3).
a_{BA}, a_{CA}	Activities of the BA and CA components in the solid phase (eqs 2, 3).
D	Distribution coefficient (eq 1).
f_B, f_C	Correction factors relating aqueous activity-fractions to the mole fractions of the total concentrations of B and C in the aqueous phase (eqs 49, 50, 51).
G	Molar Gibbs free energy of a binary solid-solution (eq 19).
G^E	Molar excess Gibbs free energy of mixing (eq 20).
G^M	Molar Gibbs free energy of mixing (eqs 20, 21).
$G^{M,id}$	Molar Gibbs free energy of mixing for an ideal solid-solution (eqs 20, 22).
IAP_{ss}	Ion activity product used to test for stoichiometric saturation with respect to a given solid (eq 4).
K_{BA}, K_{CA}	Solubility products of pure BA and pure CA solids (eqs 57, 58).
K_{ss}	Stoichiometric saturation constant for a solid $B_{1-x}C_xA$ (eq 4).
$m_{A^-}^T, m_{B^+}^T, m_{C^+}^T$	Total molalities of A, B, and C in the aqueous phase (eq 51).

n_B, n_C	Number of moles of B and C in one mole of solid $B_{1-x}C_xA$.
RT	Gas constant multiplied by the temperature in Kelvin (eq 8).
γ_{BA}, γ_{CA}	Activity coefficients of solid-phase components BA and CA (eqs 2, 3).
$\Delta\mu_r$	Free energy change of a reaction (eq 7).
$\Delta\mu_r^0$	Standard free energy change of a reaction (eq 9).
χ_{BA}, χ_{CA}	Solid-phase mole fractions of BA and CA (eqs 2, 3).
$\chi_{B,aq}$, $\chi_{C,aq}$	Activity fractions of the free B^+ and C^+ ions in the aqueous phase (eqs 41, 42).
μ_{A^-}, μ_{B^+}, μ_{C^+}	Chemical potentials of A^-, B^+, and C^+ in the aqueous phase (eq 7).
$\mu_{A^-}^0$, $\mu_{B^+}^0$, $\mu_{C^+}^0$	Standard chemical potentials of A^-, B^+, and C^+ in the aqueous phase (eq 9).
μ_{ss}	Chemical potential defined by Thorstenson and Plummer (1977) for a single component solid-solution (eq 7).
μ_{ss}^0	Standard chemical potential defined by Thorstenson and Plummer (1977) for a single component solid-solution (eq 9).
$\Sigma\Pi$	The total solubility product variable as defined by Lippmann (1977): $\Sigma\Pi = [A^-]([B^+] + [C^+])$ (eq 5).
$\Sigma\Pi_{ps}$	Value of the total solubility product for a SSAS system at primary saturation with respect to a $B_{1-x}C_xA$ solid (eq 52).
$\Sigma\Pi_{ss}$	Value of the total solubility product for a solution at stoichiometric saturation with respect to a solid $B_{1-x}C_xA$ and a given activity fraction $\chi_{B,aq}$ (see discussion of eq 56).
$\Sigma\Pi_{eq}$	Value of the total solubility product for a SSAS system at thermodynamic equilibrium with respect to a solid $B_{1-x}C_xA$ (eqs 39, 48).

LIST OF DEFINITIONS

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Activity fraction:	The ratio of the aqueous activity of one of the ions substituting in the solid-solution to the sum of the aqueous activities of the two substituting ions (see definitions of $\chi_{B,aq}$ and $\chi_{C,aq}$ in eqs 41 and 42).
Minimum stoichiometric saturation:	A stoichiometric saturation state for which $\chi_{C,aq} = x$ and $\chi_{B,aq} = 1 - x$ (for a given solid $B_{1-x}C_xA$). This state is generally close to a stoichiometric saturation state resulting from congruent dissolution of a solid-solution in initially pure water.

Primary saturation:	The first state reached during the dissolution of a solid-solution for which the aqueous phase is at saturation with respect to a secondary solid-solution.
Pure endmember saturation:	Saturation of an aqueous solution with respect to one of the endmember components of a solid-solution.
SSAS:	Solid-solution aqueous-solution.
Stoichiometric saturation:	A limiting equilibrium state, hypothesized by assuming that a solid-solution may behave as a single-component solid of invariant composition. For a binary solid-solution, the stoichiometric saturation condition is given by eq (11) or equivalently eq (14).
Thermodynamic equilibrium:	The state defined by considering the solid-solution as a multi-component solid and equating the chemical potential of each of its components to the corresponding chemical potential in the aqueous-solution. For a binary solid-solution, these conditions are given by eqs (12) and (13), or equivalently eqs (2) and (3).

THE THORSTENSON AND PLUMMER STOICHIOMETRIC SATURATION MODEL

Brief description.—While acknowledging that eqs (2) and (3) describe thermodynamic equilibrium in a binary SSAS system, Thorstenson and Plummer (1977) contend that in low-temperature geological environments, SSAS systems rarely achieve thermodynamic equilibrium. They argue instead that solid-solution compositions commonly remain invariant during solid-phase aqueous-phase reactions. In particular, solid-solutions dissolving in an aqueous-phase do not reach equilibrium in an observable time-scale. Net dissolution is instead arrested, at least momentarily, when the aqueous-phase reaches a point of "stoichiometric saturation" with respect to the solid-phase. The term "stoichiometric saturation" refers to an equilibrium state between an aqueous-phase and a solid-solution, "in situations where, owing to kinetic restrictions, the composition of the solid phase remains invariant, even though the solid phase may be a part of a continuous compositional series" (Thorstenson and Plummer, 1977).

According to Thorstenson and Plummer (1977), a mineral of composition $B_{1-x}C_xA$ upon first contact with an aqueous-phase dissolves congruently until stoichiometric saturation is reached. Then, if kinetic restrictions are removed, the mineral can dissolve incongruently (due to

a recrystallization process and/or to the precipitation of a secondary solid), thereby evolving toward thermodynamic equilibrium. Congruent dissolution of a solid-solution $B_{1-x}C_xA$ is defined as:

$$B_{1-x}C_xA \rightarrow (1-x)B^+ + xC^+ + A^- \qquad (6)$$
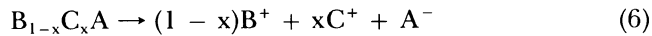
The term "congruent dissolution" only implies that the transfer of ions between the solid and aqueous phases occurs with a ratio $B^+/C^+/A^-$ equal to that of the solid.

If a solid-solution reacts while retaining a constant composition, the solid can be thermodynamically considered a one-component phase. In such a case, equating the chemical potentials of the endmember components in the various phases, such as was implicitly done in eqs (2) and (3), is invalid or at least is no longer required (Thorstenson and Plummer, 1977).

If the congruent dissolution reaction (6) proceeds to equilibrium and if temperature and pressure are constant, the free energy change $\Delta\mu_r$ of the reaction is:

$$\Delta\mu_r = (1-x)\mu_{B^+} + x\mu_{C^+} + \mu_{A^-} - \mu_{ss} = 0 \qquad (7)$$

where μ_{B^+}, μ_{C^+}, μ_{A^-}, and μ_{ss} are the respective chemical potentials of the aqueous ions B^+, C^+, A^- and the solid-solution $B_{1-x}C_xA$. Substituting definitions for the chemical potential μ_i of a component i and for the standard free energy change $\Delta\mu_r^0$ of reaction (6),

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (8)$$

$$\Delta\mu_r^0 = (1-x)\mu_{B^+}^0 + x\mu_{C^+}^0 + \mu_{A^-}^0 - \mu_{ss}^0 \qquad (9)$$

gives the following relation:

$$\Delta\mu_r^0 = -RT \ln \left(\frac{[B^+]^{1-x}[C^+]^x[A^-]}{a_{B_{1-x}C_xA}} \right) \qquad (10)$$

where $a_{B_{1-x}C_xA}$ is the activity of the $B_{1-x}C_xA$ solid.

Using the above equations and considering the solid as a one-component phase (with unit activity), Thorstenson and Plummer write an equilibrium constant expression for the congruent dissolution reaction (6):

$$K_{ss} = [B^+]^{1-x}[C^+]^x[A^-] = \exp\left(\frac{-\Delta\mu_r^0}{RT}\right) \qquad (11)$$

K_{ss}, the stoichiometric saturation *constant,* can be compared to the Ion Activity Product *variable,* $IAP_{ss} = [B^+]^{1-x}[C^+]^x[A^-]$, in order to determine whether the solution is at stoichiometric saturation with respect to a specific solid-solution $B_{1-x}C_xA$. The value of K_{ss} is depen-

dent on the standard chemical potential of the solid-solution μ_{ss}^0 (eq 9), and therefore K_{ss} will vary as a function of solid-solution composition.

Determination of the thermodynamic-mixing properties of a solid-solution from stoichiometric saturation measurements.—Thorstenson and Plummer (1977) derive equations to predict solid-phase activity coefficients and distribution coefficients at thermodynamic equilibrium if stoichiometric saturation constants are known as a function of composition. According to Thorstenson and Plummer (1977), the constraint that $IAP_{ss} = K_{ss}$ at stoichiometric saturation will be valid whether or not the phases involved are stable. The only restriction is that the composition of the solid must remain invariant. If this constraint is removed (that is if incongruent dissolution occurs), then the equilibrium criteria become those of thermodynamic equilibrium, namely $\mu_{i,a} = \mu_{i,b}$ for all components i in any two phases a and b.

Thermodynamic equilibrium for the $B_{1-x}C_xA–H_2O$ system is defined by the following relations (from which eqs (2) and (3) can be derived):

$$\mu_{A^-} + \mu_{B^+} - \mu_{BA} = 0 \tag{12}$$

$$\mu_{A^-} + \mu_{C^+} - \mu_{CA} = 0 \tag{13}$$

where μ_{BA} and μ_{CA} are the chemical potentials of the BA and CA components in the solid-solution.

If eqs (12) and (13) are multiplied by $(1 - x)$ and x respectively and summed, the following relation is obtained, still representative of thermodynamic equilibrium:

$$\mu_{A^-} + x\mu_{C^+} + (1 - x)\mu_{B^+} - [x\mu_{CA} + (1 - x)\mu_{BA}] = 0 \tag{14}$$

As pointed out by Dandurand and Schott (1980), eq (14) is a *necessary* but not a *sufficient* condition for thermodynamic equilibrium. Stoichiometric saturation, as defined in the Thorstenson and Plummer model, corresponds to *any* state that may be described by eq (14). Thermodynamic equilibrium corresponds to a state described both by eq (14) *and* either eq (12) or eq (13). Thermodynamic equilibrium, therefore, is one of a series of possible stoichiometric saturation states for which the B^+/C^+ ratio in the aqueous phase usually differs from that in the solid.

Eq (14) can be expanded in terms of standard chemical potentials and activities:

$$\mu_{A^-}^0 + x\mu_{C^+}^0 + (1 - x)\mu_{B^+}^0 - [x\mu_{CA}^0 + (1 - x)\mu_{BA}^0 + RT \ln (a_{CA}^x a_{BA}^{1-x})]$$
$$= -RT \ln ([A^-][C^+]^x[B^+]^{1-x}) \tag{15}$$

Substituting the definition of K_{ss} (eq 11) gives:

$$\mu_{A^-}^0 + x\mu_{C^+}^0 + (1 - x)\mu_{B^+}^0 - [x\mu_{CA}^0 + (1 - x)\mu_{BA}^0 + RT \ln (a_{CA}^x a_{BA}^{1-x})]$$
$$= -RT \ln K_{ss} \tag{16}$$

Eq (16) can now be compared to Thorstenson and Plummer's (1977) expression for K_{ss} as a function of $\Delta\mu_r^0$ (derived from eqs 9 and 11):

$$-RT \ln K_{ss} = \Delta\mu_r^0 = (1 - x)\mu_{B^+}^0 + x\mu_{C^+}^0 + \mu_{A^+}^0 - \mu_{ss}^0 \qquad (17)$$

The implication of this comparison is then that the standard chemical potential μ_{ss}^0 of the one component solid $B_{1-x}C_xA$, as used in Thorstenson and Plummer's description of the stoichiometric saturation model (see eqs 9 and 10), can be related to the standard chemical potentials μ_{BA}^0 and μ_{CA}^0 of the endmember components by the following equation:

$$\mu_{ss}^0 = x\mu_{CA}^0 + (1 - x)\mu_{BA}^0 + RT \ln (a_{CA}^x a_{BA}^{1-x}) \qquad (18)$$

Eq (18) is equivalent to:

$$\boxed{\begin{aligned}
\mu_{ss}^0 &= x(\mu_{CA}^0 + RT \ln a_{CA}) + (1 - x)(\mu_{BA}^0 + RT \ln a_{BA}) \\
&= x\mu_{CA} + (1 - x)\mu_{BA} = G \qquad (19)
\end{aligned}}$$

The above relation shows that the standard chemical potential μ_{ss}^0 of the single-component phase $B_{1-x}C_xA$ is equal to the molar Gibbs free energy G of the "two-component" solid-solution $B_{1-x}C_xA$ at the same temperature and pressure.

Expressions for the activities of the endmember components of $B_{1-x}C_xA$ as a function of endmember solubility products and K_{ss} values can now be found. The derivation first makes use of the relation between the excess free energy of mixing G^E, the free energy of mixing G^M of a real solution, and the free energy of mixing $G^{M,id}$ of an ideal solution (Prigogine and Defay, 1954; Swalin, 1972; Saxena, 1973; Denbigh, 1981):

$$G^E = G^M - G^{M,id} \qquad (20)$$

The free energy of mixing of a solid-solution can be considered to be the difference between the actual free energy G of the solid-solution and that of a compositionally-equivalent mechanical mixture of the endmember components:

$$G^M = x\mu_{CA} + (1 - x)\mu_{BA} - [x\mu_{CA}^0 + (1 - x)\mu_{BA}^0] \qquad (21)$$

For an ideal solid-solution, the free energy of mixing will be:

$$G^{M,id} = RT[x \ln x + (1 - x) \ln (1 - x)] \qquad (22)$$

Combining eqs (21) and (22) and relating the free energy G $(=x\mu_{CA} + (1 - x)\mu_{BA} = \mu_{ss}^0)$ of the solid-solution (in eq 21) to the stan-

dard free energy change $\Delta\mu_r^0$ of the congruent dissolution reaction (see eq 9) gives:

$$G^E = x(\mu_{C^+}^0 + \mu_{A^-}^0 - \mu_{CA}^0) + (1 - x)(\mu_{B^+}^0 + \mu_{A^-}^0 - \mu_{BA}^0) - \Delta\mu_r^0$$
$$-RT[x \ln x + (1 - x) \ln (1 - x)] \quad (23)$$

which is equivalent to:

$$G^E = RT[\ln K_{ss} - x(\ln K_{CA} + \ln x)$$
$$- (1 - x)(\ln K_{BA} + \ln (1 - x))] \quad (24)$$

The equations expressing the relation between the excess free energy of a solid-solution and the activity coefficients of its components are (Saxena, 1973, p. 15):

$$RT\ln\gamma_{BA} = G^E - x\frac{\partial G^E}{\partial x} \quad (25)$$

$$RT\ln\gamma_{CA} = G^E + (1 - x)\frac{\partial G^E}{\partial x} \quad (26)$$

The above equations can be derived from an alternate definition of the excess free energy (which follows from eq 20)

$$G^E = RT \Sigma n_i \ln \gamma_i \quad (27)$$

which implies from the Gibbs-Duhem equation (Denbigh, 1981, p. 286) that

$$dG^E = RT \Sigma \ln \gamma_i dn_i \quad (28)$$

or

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j} = RT \ln \gamma_i \quad (29)$$

To evaluate eqs (25) and (26), the derivative of G^E with respect to x must first be determined:

$$\frac{\partial G^E}{\partial x} = RT \left[\frac{\partial \ln K_{ss}}{\partial x} + \ln\left(\frac{K_{BA}}{K_{CA}}\right) + \ln \frac{(1 - x)}{x}\right] \quad (30)$$

Substituting eqs (24) and (30) into eqs (25) and (26) respectively gives the following equations for the activity coefficients of the BA and CA components:

$$\ln \gamma_{BA} = -x \frac{\partial}{\partial x} (\ln K_{ss}) + \ln K_{ss} - \ln K_{BA} - \ln (1 - x) \quad (31)$$

$$\ln \gamma_{CA} = (1 - x)\frac{\partial}{\partial x}(\ln K_{ss}) + \ln K_{ss} - \ln K_{CA} - \ln x \quad (32)$$

which are equivalent to the equations first derived by Thorstenson and Plummer (1977):

$$\log a_{BA} = -x\frac{\partial}{\partial x}(\log K_{ss}) + \log K_{ss} - \log K_{BA} \quad (33)$$

$$\log a_{CA} = (1 - x)\frac{\partial}{\partial x}(\log K_{ss}) + \log K_{ss} - \log K_{CA} \quad (34)$$

Solid-phase activity-coefficients for given solid compositions can be calculated from measured K_{ss} and estimated $\partial K_{ss}/\partial x$ data, as Thorstenson and Plummer (1977) and Plummer and Busenberg (1987) suggested. Alternatively, activity coefficients and other thermodynamic properties can be calculated by directly converting K_{ss} data to G^E data (through eq 24) and then using a fitting model for G^E as a function of composition. Guggenheim's expansion series for G^E (Guggenheim, 1937; Redlich and Kister, 1948; King, 1969) is currently one of the most popular models used to describe solid-solutions and non-aqueous liquid solutions:

$$G^E = \chi_{CA}\chi_{BA}RT[a_0 + a_1(\chi_{CA} - \chi_{BA}) + a_2(\chi_{CA} - \chi_{BA})^2 + \ldots] \quad (35)$$

The Guggenheim model is functionally equivalent (see Glynn, 1989b) to the Thompson and Waldbaum (1969) model (a two parameter model used in igneous petrology) and to the original Margules activity-coefficient fitting series (Margules, 1895; Prigogine and Defay, 1954). Other possible G^E fitting functions include Guggenheim's (1952) quasi-chemical model, the Van Laar model (Carlson and Colburn, 1942), and the Wilson (1964) model. G^E calculation and estimation techniques are further discussed by Glynn (1989a, b).

Once activity coefficients are measured or estimated (using K_{ss} data) as a function of solid composition, distribution coefficients at thermodynamic equilibrium can be predicted (see eq 32 in Thorstenson and Plummer, 1977). The composition of the solid-solution at thermodynamic equilibrium will generally differ, however, from the composition of the initial solid on which the stoichiometric saturation measurement was conducted. Therefore, the measurement of a stoichiometric saturation state for a given SSAS system with initial solid composition $B_{1-x}C_xA$ will not, by itself, define the composition of the system at thermodynamic equilibrium. The only exceptions will occur in the case of a SSAS system with an *infinite* solid to solution ratio (and a thermodynamically-stable initial solid) and in special cases where the measured stoichiometric saturation state actually corresponds to thermodynamic equilibrium. This effect of the initial solid to solution ratio on the final composition of a SSAS system at thermodynamic equilibrium has been

discussed extensively by Glynn and others (1990), Denis and Michard (1983), Michard and Ouzoukian (1978), and Wollast and Reinhard-Derie (1977).

Finally, in the case where solid-phase component activities are known or can be estimated as a function of composition, K_{ss} values can be directly calculated, for any given solid-composition $B_{1-x}C_xA$, through the following relation:

$$K_{ss} = K_{CA}^x K_{BA}^{(1-x)} a_{CA}^x \, a_{BA}^{(1-x)} \qquad (36)$$

This equation can be derived from eq (16) and is equivalent to Thorstenson and Plummer's (1977) eq (22).

Criticisms of the Thorstenson and Plummer model.—Criticisms offered by Lafon (1978), Gresens (1981a, b), and Lippmann (1977) concerning the Thorstenson and Plummer stoichiometric saturation model or more generally the K_{ss} formulation are reviewed in the appendix. While we agree with Lafon's arguments against the applicability of the stoichiometric saturation concept to precipitation processes, we believe that the criticisms offered do not invalidate the use of the stoichiometric saturation concept in the interpretation of solid-solution dissolution experiments.

THE LIPPMANN TOTAL SOLUBILITY PRODUCT MODEL

Description of the Lippmann model.—Lippmann argues that solubility expressions for solid-solutions should not be derived by simply considering stoichiometric dissolution. Instead, he suggests using the fundamental law of equilibrium thermodynamics, $\mu_{i,a} = \mu_{i,b}$, valid for any component i distributed between two phases a and b at thermodynamic equilibrium and at constant temperature and pressure. For a SSAS system with two solid-phase components, BA and CA, this law translates into the mass action relations given in eqs (2) and (3).

If eqs (2) and (3) hold true at thermodynamic equilibrium, so must their sum or any other arithmetic combination. This principle was used by Delaney and Nash (1977), who proposed an equilibrium constant derived by multiplying eqs (2) and (3) by each other. The same principle is inherent in the Thorstenson and Plummer model, where K_{ss} can be defined by raising eqs (2) and (3) to the x and $(1 - x)$ powers respectively and multiplying them together (see eq 36). Using an analogy to binary liquid-vapor systems, Lippmann adds eqs (2) and (3) together:

$$(|B^+| + |C^+|)[A^-] = a_{BA} K_{BA} + a_{CA} K_{CA} \qquad (37)$$

Lippmann then defines the "total solubility product" variable $\Sigma\Pi$

$$\Sigma\Pi = (|B^+| + |C^+|)[A^-] \qquad (38)$$

such that at thermodynamic equilibrium, Lippmann's $\Sigma\Pi_{eq}$ versus χ_{BA} curve or "solidus curve" is given by:

$$\Sigma\Pi_{eq} = a_{BA}K_{BA} + a_{CA}K_{CA} = \chi_{BA}\gamma_{BA}K_{BA} + \chi_{CA}\gamma_{CA}K_{CA} \qquad (39)$$

($\Sigma\Pi_{eq}$ refers to the value of $\Sigma\Pi$ as specifically defined at thermodynamic equilibrium).

In the case of an ideal solid-solution, component activities are equal to component mole-fractions and eq (39) becomes:

$$\Sigma\Pi_{eq} = \chi_{BA}K_{BA} + \chi_{CA}K_{CA} = K_{CA} + \chi_{BA}(K_{BA} - K_{CA}) \qquad (40)$$

Eq (40) is equivalent to an equation derived by Berndt and Stearns (1973) for the solubility of an ideal solid-solution and is also analogous (see Lippmann, 1980) to the "isothermal vaporization" curve for a binary liquid-gas system (Prigogine and Defay, 1954, p. 353).

Similar to Thorstenson and Plummer's stoichiometric-saturation *constant*, K_{ss}, the value of the $\Sigma\Pi_{eq}$ *constant* is dependent on the composition of the solid-solution. However, unlike Thorstenson and Plummer's IAP_{ss} *variable* (which has mole-fraction exponents), the $\Sigma\Pi$ *variable* does not depend on the solid-phase composition. Like the stoichiometric saturation constant K_{ss}, $\Sigma\Pi_{eq}$ can be calculated (using eq 39), if the individual activities of the components in the solid phase are known at thermodynamic equilibrium.

Alternatively, $\Sigma\Pi_{eq}$ can be calculated if the activity fractions of the substituting ions in the aqueous phase are known at thermodynamic equilibrium. The activity fractions are defined as:

$$\chi_{B,aq} = \frac{[B^+]}{[C^+] + [B^+]} \qquad (41)$$

and

$$\chi_{C,aq} = \frac{[C^+]}{[C^+] + [B^+]} \qquad (42)$$

Substituting these two relations into eqs (2) and (3):

$$\frac{\chi_{B,aq}([B^+] + [C^+])[A^-]}{K_{BA}} = a_{BA} \qquad (43)$$

$$\frac{\chi_{C,aq}([B^+] + [C^+])[A^-]}{K_{CA}} = a_{CA} \qquad (44)$$

In the special case of an ideal solid-solution ($a_{BA} = \chi_{BA}$ and $a_{CA} = \chi_{CA}$), eqs (43) and (44) can be added together and rearranged. Given that $\Sigma\Pi = [A^-]\,([B^+] + [C^+])$ and knowing that $\chi_{BA} + \chi_{CA} = 1$ in a binary system, Lippmann's "solutus" expression can be derived:

$$\Sigma\Pi_{eq} = 1 \left/ \left(\frac{\chi_{B,aq}}{K_{BA}} + \frac{\chi_{C,aq}}{K_{CA}}\right) \right. = \frac{K_{CA}}{\left(1 - \chi_{B,aq}\left(1 - \frac{K_{CA}}{K_{BA}}\right)\right)} \qquad (45)$$

As pointed out by Lippmann (1980), eq (45) is analogous to the "isothermal condensation curve" for a binary liquid-phase/gas-phase system (Prigogine and Defay, 1954, p. 353):

An expression of Lippmann's solutus curve may also be obtained for the more general case of non-ideal solid-solutions by expressing the activities of the solid phase components in terms of activity coefficients and mole fractions and re-arranging eqs (43) and (44):

$$\frac{\chi_{B,aq}([B^+] + [C^+])[A^-]}{K_{BA}\gamma_{BA}} = \chi_{BA} \tag{46}$$

$$\frac{\chi_{C,aq}([B^+] + [C^+])[A^-]}{K_{CA}\gamma_{CA}} = \chi_{CA} \tag{47}$$

and adding eqs (46) and (47) together:

$$\Sigma\Pi_{eq} = 1 \left/ \left(\frac{\chi_{B,aq}}{K_{BA}\gamma_{BA}} + \frac{\chi_{C,aq}}{K_{CA}\gamma_{CA}} \right) \right. \tag{48}$$

where γ_{CA} and γ_{BA} are the activity coefficients for the equilibrium solid-phase.

Lippmann's solidus and solutus curves can be plotted and used to predict the solubility of any solid-solution at thermodynamic equilibrium, if solid-phase and aqueous-phase activity coefficients are known. Figure 1, which will be called a Lippmann phase diagram, shows an example for an ideal solid-solution series. Similar to the phase diagrams used for binary-solid/binary-melt and binary-liquid/binary-vapor systems, horizontal tie-lines can be drawn between the solutus and solidus curves thereby giving the solid-phase and aqueous-phase compositions for the series of possible thermodynamic equilibrium states. An aqueous speciation and activity coefficient model is required, however, in order to determine aqueous-phase compositions (and solid-solution solubilities). Indeed, unlike more traditional phase diagrams, there are really two x-axis scales superimposed one upon another: one applies to the solidus curve and is a mole-fraction scale ($\chi_{BA} = n_B/(n_B + n_C)$), the other is an activity-fraction scale ($\chi_{B,aq} = [B^+]/([B^+] + [C^+])$) and applies to the solutus curve and to aqueous-solution compositions in general. Aqueous solutions that plot below the solutus curve are undersaturated with respect to any solid phase, including the pure endmember solids, whereas solutions plotting above the solutus are supersaturated with respect to a series of solid-solutions.

Lippmann phase diagrams illustrate the greatest difference between the Lippmann (1977, 1980) and the Thorstenson and Plummer (1977) models. While the Lippmann model combines eqs (2) and (3) into two algebraically-different relations (the solidus and solutus equations) describing thermodynamic equilibrium and by so doing does not lose any of the information or specificity present in eqs (2) and (3), the Thorstenson and Plummer stoichiometric saturation model combines
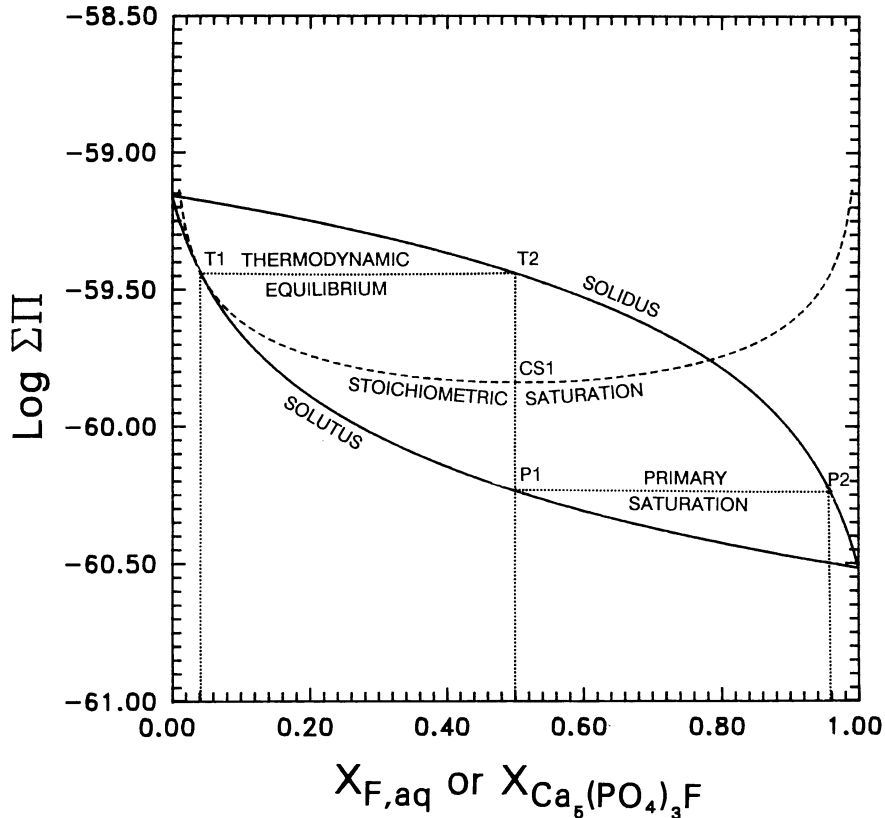
Fig. 1. Lippmann solidus and solutus curves for the $Ca_5(PO_4)_3(OH, F)-H_2O$ system at $25°C$, assuming an ideal solid-solution. Endmember pK's are 59.16 for hydroxyapatite and 60.52 for fluoroapatite (Moreno and others, 1977). The dotted horizontal tie-lines indicate the relation between the solid mole-fractions and the aqueous activity-fractions at thermodynamic equilibrium (points T2, T1) or at primary saturation (points P2, P1) with respect to a $Ca_5(PO_4)_3OH_{0.5}F_{0.5}$ solid ($B_{1-x}C_xA$ in the text). The dashed curve gives the series of possible ($\chi_{F,aq}$, $\Sigma\Pi_{ss}$) aqueous-compositions that satisfy the condition of stoichiometric saturation with respect to a $Ca_5(PO_4)_3OH_{0.5}F_{0.5}$ solid. Point CS1 is the "minimum stoichiometric saturation" point for a $Ca_5(PO_4)_3OH_{0.5}F_{0.5}$ solid.

eqs (2) and (3) into a single equation, thereby allowing a greater number of states (including thermodynamic equilibrium states) to be described.

Although Lippmann (1977, 1980, 1982a, b) originally intended his model to describe only thermodynamic equilibrium states, his $\Sigma\Pi$ formulation and his phase diagrams can be used to describe many other thermodynamic states such as primary saturation, stoichiometric saturation, and pure-endmember saturation states.

Primary saturation states: prediction and depiction on Lippmann diagrams.—Primary saturation has been described, by Wollast and Reinhard-Derie (1977), Garrels and Wollast (1978), and Denis and

Michard (1983), as the *first* state reached during the congruent dissolution of a solid-solution, for which the aqueous-solution is at saturation with respect to a secondary solid-phase. This secondary solid will usually be of different composition than that of the dissolving solid. For some special cases, namely in the case of dissolution of the pure endmembers or of an alyotropic composition (see discussion of figs. 5 and 6 in this paper; see also Lippmann, 1980), the secondary solid composition will be identical to that of the initial solid, that is, primary saturation will coincide with thermodynamic equilibrium and stoichiometric saturation with respect to the initial solid. For all other situations, primary saturation will correspond to a metastable equilibrium state, such that the aqueous phase may be considered to be at equilibrium with respect to a secondary solid, but not with respect to the primary dissolving solid phase. The series of possible primary-saturation states for a given SSAS system is represented by the solutus curve on a Lippmann diagram.

In the specific case of congruent dissolution occurring in an aqueous-phase initially free of B^+ and C^+ ions, primary-saturation can be approximately found by drawing a straight vertical line on the Lippmann diagram from the solid-phase composition to the solutus. This assumes that the ratio of the total aqueous concentrations of B and C, $m_{B^+}^T/m_{C^+}^T$, can be considered equal to the aqueous activity ratio of the B^+ and C^+ ions. This assumption will not hold if the aqueous activity coefficients of B^+ and C^+ differ from each other or if aqueous ion association (of B^+ and C^+) occurs. In such a case, the following relations may be used to determine exactly the primary saturation state:

$$\chi_{B,aq} = \frac{[B^+]}{[B^+] + [C^+]} = f_B \chi_{BA} \qquad (49)$$

$$\chi_{C,aq} = \frac{[C^+]}{[B^+] + [C^+]} = f_C \chi_{CA} \qquad (50)$$

where f_B and f_C are factors correcting for a possible difference in the ion association and in the aqueous activity coefficients of B^+ and C^+. χ_{BA} and χ_{CA} represent the composition of the primary dissolving solid $B_{1-x}C_xA$. For example,

$$f_B = \chi_{B,aq} \Big/ \left(\frac{m_{B^+}^T}{m_{B^+}^T + m_{C^+}^T} \right) \qquad (51)$$

f_B and f_C may be evaluated using any appropriate speciation model and aqueous activity theory (Debye-Hückel, 1923; Davies, 1962; Pitzer, 1979; et cetera). The equation used to calculate the value of $\Sigma\Pi$ at primary saturation as a function of solid composition, for the case of congruent dissolution in an aqueous-phase initially free of B^+ and C^+ ions, may be found by combining the Lippmann solutus (eq 48) with eqs (49) and (50):

$$\Sigma\Pi_{ps} = 1 \left/ \left(\frac{\chi_{BA}f_B}{K_{BA}\gamma_{BA,y}} + \frac{\chi_{CA}f_C}{K_{CA}\gamma_{CA,y}} \right) \right. \tag{52}$$

where $\gamma_{BA,y}$ and $\gamma_{CA,y}$ refer to the activity coefficients of BA and CA in the solid $B_{1-y}C_yA$ with respect to which the aqueous solution (at primary saturation) is in temporary thermodynamic equilibrium. $\Sigma\Pi_{ps}$ refers to the value of the $\Sigma\Pi$ variable as specifically defined at primary saturation.

The composition of the $B_{1-y}C_yA$ phase with respect to which the solution is in temporary thermodynamic equilibrium will generally not be known *a priori*. Applying the solidus expression gives:

$$\Sigma\Pi_{eq} = \chi_{CA,y}\gamma_{CA,y}K_{CA} + \chi_{BA,y}\gamma_{BA,y}K_{BA} \tag{53}$$

By equating $\Sigma\Pi_{ps}(x)$ (eq 52) to $\Sigma\Pi_{eq}(y)$ (eq 53), the following relation between the initial solid composition $B_{1-x}C_xA$ and the secondary solid $B_{1-y}C_yA$ may be obtained:

$$1 \left/ \left(\frac{\chi_{BA}f_B}{K_{BA}\gamma_{BA,y}} + \frac{\chi_{CA}f_C}{K_{CA}\gamma_{CA,y}} \right) \right. = \chi_{CA,y}\gamma_{CA,y}K_{CA} + \chi_{BA,y}\gamma_{BA,y}K_{BA} \tag{54}$$

The above equation will be easy to use in the case of an ideal solid-solution series. In the general case of a non-ideal solid-solution series, eq (54) will be transcendental in $\chi_{CA,y}$ (because $\gamma_{BA,y}$ and $\gamma_{CA,y}$ are typically exponential functions of $\chi_{CA,y}$), and if the secondary solid composition is desired, eq (54) will have to be solved graphically or by an iterative technique.

Stoichiometric saturation and pure endmember saturation states: prediction and depiction on Lippmann diagrams.—The Thorstenson and Plummer model and the Lippmann model seem very different in their formulation of "equilibrium" constants. Indeed, the constant of stoichiometric saturation K_{ss} and the total solubility product $\Sigma\Pi_{eq}$ were initially intended for very different purposes, one as a predictor of stoichiometric saturation, the other as a predictor of thermodynamic equilibrium. Nevertheless, the *variables* IAP_{ss} and $\Sigma\Pi$ can be related to each other and can both be used to describe stoichiometric saturation or thermodynamic equilibrium states.

Multiplying the definition of IAP_{ss} (eq 4) by $([B^+] + [C^+])/([B^+] + [C^+])$ gives:

$$IAP_{ss} = [A^-]([B^+] + [C^+]) \left(\frac{[B^+]}{[B^+] + [C^+]} \right)^{1-x} \left(\frac{[C^+]}{[B^+] + [C^+]} \right)^x \tag{55}$$

Substituting Lippmann's definitions of the $\Sigma\Pi$ and $\chi_{B,aq}$ and $\chi_{C,aq}$ variables in eq (55) gives the following relation between $\Sigma\Pi$ and IAP_{ss}:

$$\Sigma\Pi = \frac{IAP_{ss}}{\chi_{B,aq}^{1-x}\chi_{C,aq}^x} \tag{56}$$

In contrast to thermodynamic equilibrium, which is constrained to a single $(\chi_{B,aq}, \Sigma\Pi_{eq})$ point by eqs (2) and (3) (for a given equilibrium solid composition), stoichiometric saturation is represented by a series of $\chi_{B,aq}, \Sigma\Pi_{ss})$ points (fig. 1), defined by eq (56) and by the condition $IAP_{ss} = K_{ss}$. In plotting the series of stoichiometric saturation states for a given solid-solution $B_{1-x}C_xA$, the mole-fractions x and $1-x$ are held constant in eq (56), and $\chi_{B,aq}$ (and $\chi_{C,aq}$) are allowed to vary from 0 to 1. As shown in figure 1, stoichiometric saturation states never plot below the solutus curve. This phenomenon is consistent with the fact that stoichiometric saturation can never be reached *before* primary saturation in a solid-solution dissolution experiment. The unique point at which a stoichiometric saturation curve joins the Lippmann solutus represents the composition of an aqueous solution at thermodynamic equilibrium with respect to a solid $B_{1-x}C_xA$.

Stoichiometric saturation curves all have a characteristic minimum $\Sigma\Pi$ value at the "minimum stoichiometric saturation" point. We define this point as a stoichiometric saturation state that meets the conditions $\chi_{B,aq} = 1-x (=\chi_{BA})$ and $\chi_{C,aq} = x (=\chi_{CA})$ in eq (56). This state can often be approximated as the stoichiometric saturation state resulting from the congruent dissolution of a solid-solution in initially pure water. A "minimum stoichiometric saturation" curve can be constructed from the series of "minimum stoichiometric saturation" points and used to portray the dependence of the $\Sigma\Pi_{ss}$ constant on solid composition. The curve can be used in conjunction with thermodynamic equilibrium points to sketch any particular stoichiometric saturation curve on a Lippmann diagram. As later illustrated (figs 7, 8), the "minimum stoichiometric saturation" curve can also be used to test the closeness of fit between experimental stoichiometric saturation data and a given excess-free-energy model for a solid-solution series.

Saturation curves for the BA and CA endmember solids can also be drawn on Lippmann diagrams by applying the two limiting situations $x = 0$ and $x = 1$ to eq (56) and to eq (36) which defines K_{ss} as a function of K_{BA} and K_{CA}:

$$\Sigma\Pi_{BA} = \frac{K_{BA}}{\chi_{B,aq}} \tag{57}$$

and

$$\Sigma\Pi_{CA} = \frac{K_{CA}}{\chi_{C,aq}} \tag{58}$$

These equations, also given by Lippmann (1980, 1982, b), define the families of $(\chi_{B,aq}, \Sigma\Pi_{BA})$ and $(\chi_{C,aq}, \Sigma\Pi_{CA})$ conditions for which a solution containing A^-, B^+, and C^+ ions will be at saturation with respect to pure BA and pure CA solids.

For most purposes, the stoichiometric saturation concept can be seen as a generalization of the classical pure-phase solubility-product

theory. Both concepts consider the solid as a phase of fixed composition. The Gibbs phase rule predicts 0 degrees of freedom for both stoichiometric saturation and pure endmember saturation states (assuming that at stoichiometric saturation the system can be considered to have only two components, H_2O and $B_{1-x}C_xA$). As a consequence, and in contrast to the thermodynamic equilibrium states described by the Lippmann model (3 components − 2 phases = 1 degree of freedom), stoichiometric saturation and pure endmember saturation states will be independent of the initial solid to solution mass ratio (Glynn and others, 1990). Indeed, the initial pre-equilibration composition of a solid-solution will in general differ from that of the final solid at thermodynamic equilibrium. Therefore, the final solid composition will in general depend on the initial solid to solution ratio. The only exception to this rule will occur in
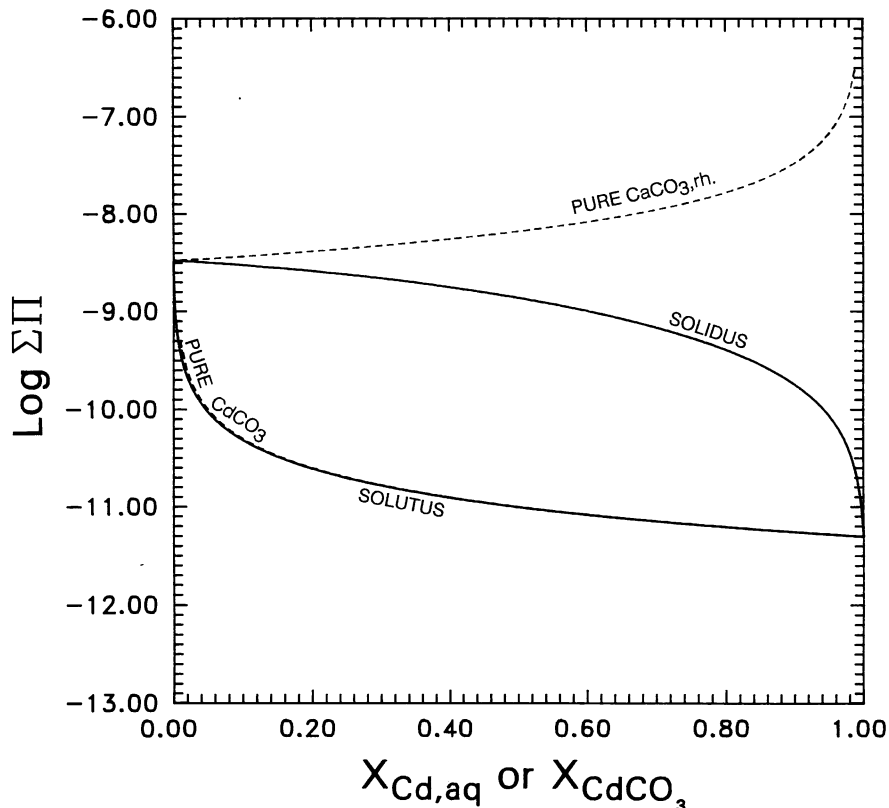

Fig. 2. Lippmann phase diagram for the $(Ca, Cd)CO_3–H_2O$ system at 25°C drawn using the Cd-in-calcite distribution coefficient data and $CdCO_3$ solubility data of Davis and others (1987), assuming a regular solid-solution model ($a_0 = -0.8$). Endmember pK's are 8.48 for calcite (Plummer and Busenberg, 1982) and 11.31 for otavite. Dashed lines represent endmember saturation curves.

situations for which thermodynamic equilibrium is reached simultaneously with primary saturation.

One difference between stoichiometric saturation and pure endmember saturation states can be seen by comparing eqs (56) and (57). For values of x tending (but not equal) to 0 or 1, $\Sigma\Pi_{ss}$ values will tend to $+\infty$ at $\chi_{BA} = 0$ or $\chi_{CA} = 0$. In contrast, pure endmember saturation curves are asymptotic for $\chi_{BA} = 0$ or $\chi_{CA} = 0$ but not for both conditions. The reason for the asymptotic behavior of both the pure endmember and stoichiometric saturation curves is that as $[B^+]$ (or $[C^+]$) goes to 0, the value of $[A^-]$ must tend to $+\infty$ in order to maintain the various saturation conditions ($IAP_{BA} = K_{BA}$, $IAP_{CA} = K_{CA}$, $IAP_{SS} = K_{ss}$). Unlike the stoichiometric saturation and pure endmember saturation curves, Lippmann's solutus does not exhibit any "infinite solubility" points.

Comparison of pure endmember saturation curves with Lippmann solutus curves.—As demonstrated above, Lippmann diagrams can be used to depict not only thermodynamic equilibrium and primary saturation states but also stoichiometric saturation and pure endmember saturation states. As a consequence, Lippmann diagrams can be used to determine whether a solid-aqueous phase system may be described with sufficient accuracy by conventional solubility theory or whether a more complex solid-solution aqueous-solution model may be needed.

A nearly ideal solid-solution series ((Ca, Cd)CO_3) is shown in figure 2. The endmember solubility products in this system differ by almost three orders of magnitude. The solutus curve and the curve representing saturation with respect to the $CdCO_3$ endmember closely follow each other except in the region where $\chi_{Cd,aq}$ is close to 0. In that region, the pure $CdCO_3$ curve approaches an infinitely high value of $\Sigma\Pi$, while the solutus curve intercepts the $\Sigma\Pi$ axis at a value equal to the pure $CaCO_{3,rh}$ solubility product. The pure $CaCO_{3,rh}$ curve is consistently above the solutus (except at $\chi_{CaCO_3} = 1$); therefore a solution at thermodynamic equilibrium with respect to any (Ca, Cd)CO_3 solid will always be undersaturated with respect to pure $CaCO_{3,rh}$. Such a solution will also always be undersaturated with respect to pure $CdCO_3$, but in this case only by a very small amount. Recall the definition of the solutus curve:

$$\Sigma\Pi_{eq} = 1 \left/ \left(\frac{\chi_{B,aq}}{K_{BA}\gamma_{BA}} + \frac{\chi_{C,aq}}{K_{CA}\gamma_{CA}} \right) \right. \tag{48}$$

If the value of K_{CA} ($K_{CaCO_3,rh}$ in the above example) is considerably greater than that of K_{BA} (K_{CdCO_3}) and if the solid-phase activity coefficients are unity (case of an ideal solid-solution), the term $\chi_{C,aq}/(K_{CA}\gamma_{CA})$ will be insignificant compared to the value of $\chi_{B,aq}/(K_{BA}\gamma_{BA})$, and the solutus equation will essentially be identical to the pure BA ($CdCO_3$) solubility curve, except at values of $\chi_{B,aq}$ very close to zero.

Figure 3 represents the case of a non-ideal SSAS system, (Ca,Zn)CO_3-H_2O, with an order of magnitude difference in endmember solubility products and with a miscibility gap between $\chi_{ZnCO_3} = 0.20$ and
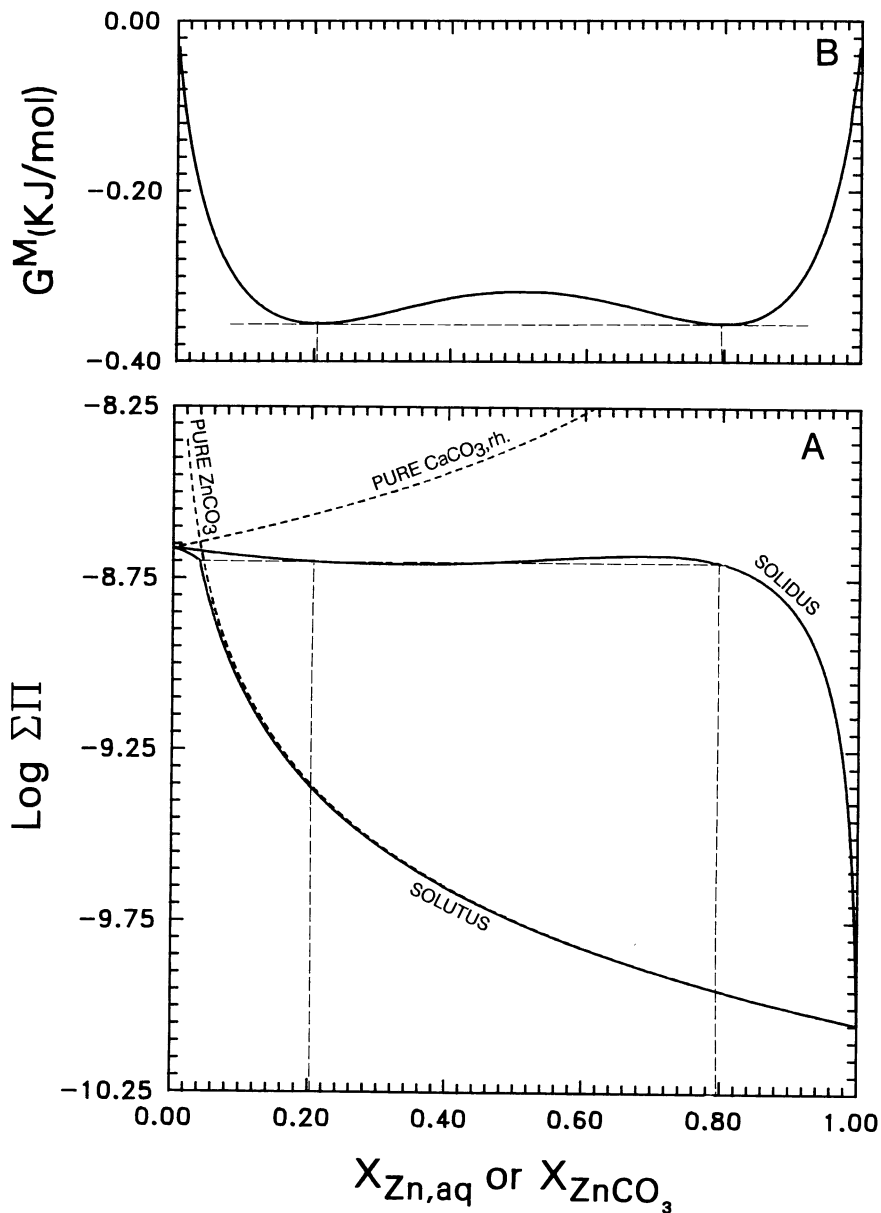
Fig. 3(A) Lippmann phase diagram for the (Ca, Zn)CO_3–H_2O system at 50°C drawn using the Zn-in-calcite distribution coefficient results of Crocket and Winchester (1966) and assuming a regular solid-solution (a_0 = 2.3). Endmember pK's chosen are 8.663 for calcite (Plummer and Busenberg, 1982) and 10.05 for smithsonite (Högfeldt, 1982). The calculated miscibility gap (from χ_{ZnCO3} = 0.20 to 0.80) is in reasonable agreement with the maximum amount of Ca in smithsonite (χ_{CaCO3} = 0.24) reported by Palache, Berman, and Frondel (1951). Short-dashed lines represent endmember saturation curves. Long-dashed lines show the miscibility gap determined from the intersection of the solidus curve with a straight horizontal line drawn from the "peritectic" point. (B) Gibbs free energy of mixing for the (Ca, Zn)CO_3–H_2O system as a function of composition. The long-dashed lines show the miscibility gap determined from the common tangent points of the G^M curve. The inflexion points give the spinodal gap compositions, which can also be found from the two local extrema in the Lippmann solidus curve.

χ_{ZnCO_3} = 0.80. Whereas the solidus curve differs from that of the (Ca,Cd)CO$_3$ system, the solutus curve remains very close to the pure ZnCO$_3$ saturation curve. This behavior is due to the narrow range of solid-solution compositions at equilibrium with respect to the aqueous-solution compositions defined by the solutus curve. The solid-phase activity-coefficients in the solutus expression depend on the equilibrium solid compositions. Because the range of solid compositions is small and close to pure ZnCO$_3$ (from χ_{ZnCO_3} = 0.80 to χ_{ZnCO_3} = 1.0), the activity coefficients do not vary significantly, and the solutus curve, therefore, remains unchanged and almost identical to the pure ZnCO$_3$ saturation curve. Indeed, the values of the CaCO$_{3,rh}$ and ZnCO$_3$ activity coefficients have a certain limit which when exceeded (between χ_{ZnCO_3} = 0.20 and χ_{ZnCO_3} = 0.80) results in unstable or metastable solid-solutions (with respect to which an aqueous-solution can never reach thermodynamic equilibrium). The upper limit placed on the solutus curve by the endmember saturation curves can also be explained by the fact that a pure endmember phase will always have a higher free energy than a solid-phase with some non-zero proportion of substitutional impurities (Berry and others, 1980, p. 1110). Increasing the excess free energy of a solid-solution series (such as by increasing the a$_0$ value in eq 35) causes a miscibility gap to form and then to broaden with its limits tending toward the pure endmember compositions. In corresponding behavior, the Lippmann solutus curve will move upward, closer and closer to the pure-phase saturation curves, but never crossing their boundaries.

If the endmember solubility products are close, the solutus curve is in equilibrium with a much more evenly distributed range of solid-compositions, and the solutus and solidus curves plot near each other. In the Ba(CrO$_4$, SO$_4$)–H$_2$O system (fig. 4), endmember solubility products differ by about 0.4 log $\Sigma\Pi$. The Ba(CrO$_4$, SO$_4$) solid-solutions are assumed ideal. In this case, the pure-phase solubility curves are quite distinct from the solutus, and solution compositions along the solutus are clearly undersaturated with respect to both pure BaSO$_4$ and pure BaCrO$_4$ solids.

A hypothetical example of a system with a negative excess free energy of mixing is illustrated in figure 5. Because a negative excess free energy lowers the position of a solutus curve relative to the position of an ideal solutus, the solutus in this system lies distinctly below the pure BA saturation curve. The system also shows an alyotropic minimum, a point of intermediate composition corresponding to a minimum in the solidus curve. By definition (Schuberth, 1977; Lippmann, 1980), an alyotropic point is a thermodynamic equilibrium state with a B$^+$/C$^+$ ratio in the solid phase equal to the $m_{B^+}^T/m_{C^+}^T$ ratio in the aqueous phase. The alyotropic minimum in figure 5 is a result of the strong attraction between the two components of the solid-solution.

If the excess free energy of mixing is non-zero and positive, and if the endmember solubility products are close together, a SSAS system may exhibit an alyotropic maximum, such as can be seen for example in
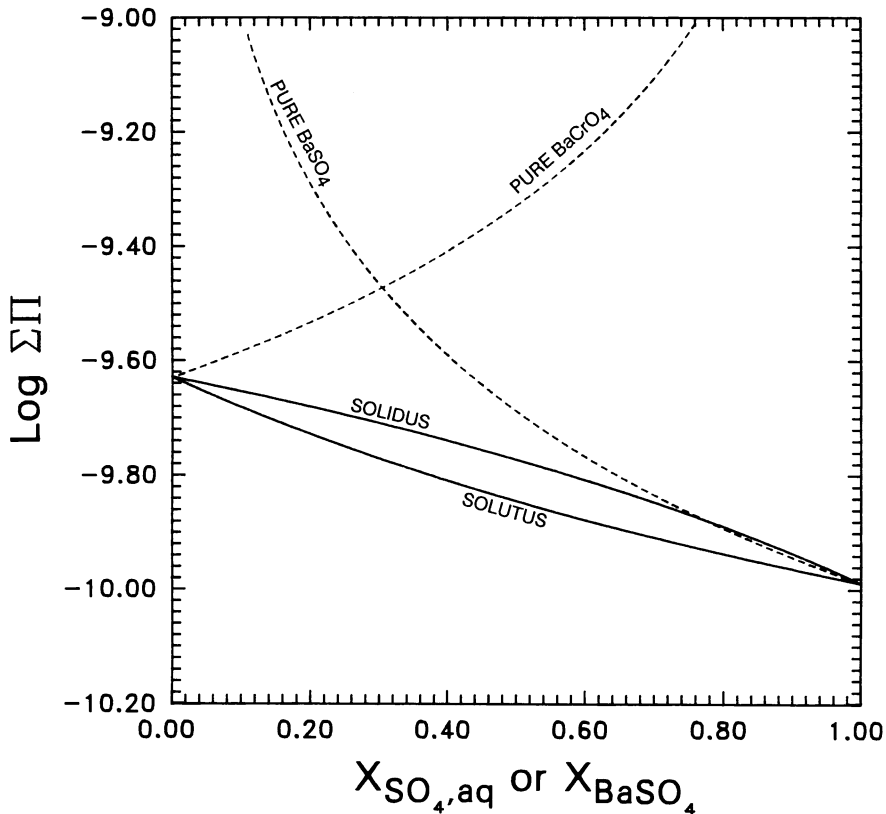
Fig. 4. Lippmann phase diagram for the $Ba(CrO_4, SO_4)-H_2O$ system at $25°C$, assuming an ideal solid-solution series. Endmember pK's chosen are 9.67 for $BaCrO_4$ (Lukkari and Lukkari, 1972) and 9.99 for $BaSO_4$ (Högfeldt, 1982).

the $K(Cl, Br)-H_2O$ system (fig. 6). In such a system, the excess free energy of mixing is not sufficiently high to cause the formation of a miscibility gap. The solutus curves upward toward the alyotropic point and, in doing so, tends close to the pure-phase solubility curves. In this system, as in all systems discussed above, the pure endmember saturation curves offer an upward boundary for the solutus curve.

Criticisms of the Lippmann model.—The principal limitation of Lippmann's Total Solubility Product model is its inherent assumption that solid phases can behave as compositionally uniform phases and attain thermodynamic equilibrium in an aqueous solution. At low temperatures, solids often behave as multi-compositional phases and are not very responsive to changes in the surrounding aqueous phase composition. Thorstenson and Plummer (1977) developed the concept of stoichiometric saturation, claiming that solid-solution compositions could
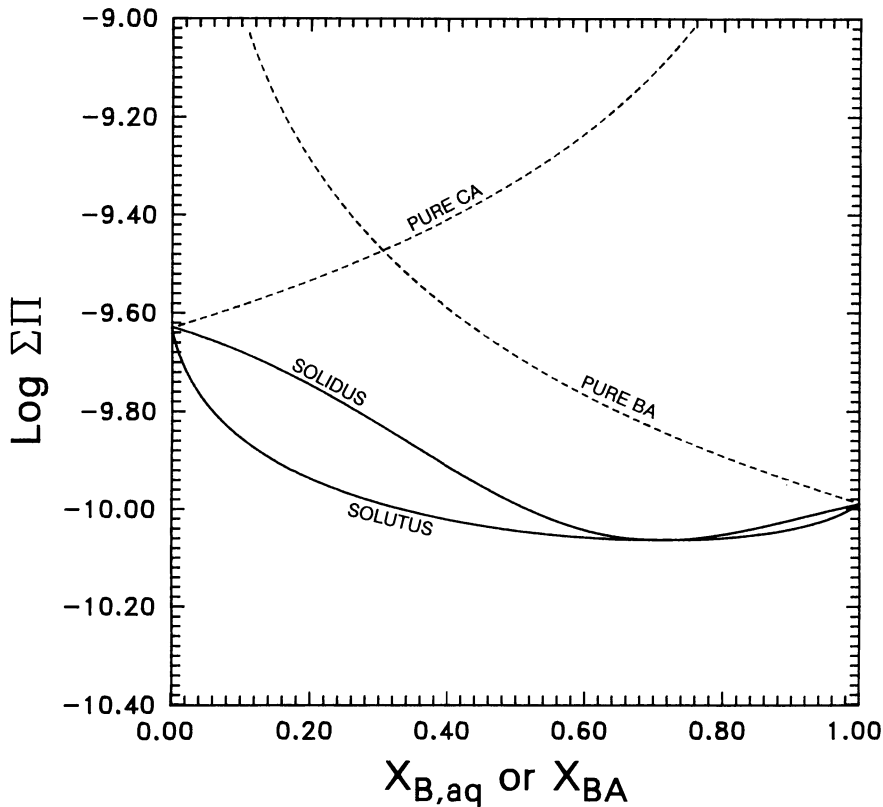
Fig. 5. Lippmann phase diagram for a hypothetical SSAS system with close endmember solubility products (pK_{CA} = 9.67, pK_{BA} = 9.99) and an alyotropic minimum (a_0 = −2.).

remain invariant for extended periods of time. It must be emphasized, however, that the stoichiometric saturation concept can also be applied only if the initial solid dissolved is compositionally homogeneous and if the rate of precipitation of any secondary phases is slow compared to the rate of dissolution.

Lippmann's formulation of the $\Sigma\Pi$ variable has not met many objections in the literature, with the possible exception of Walter and Morse (1984). Walter and Morse claimed that, unlike Thorstenson and Plummer's (1977) K_{ss} constant, $\Sigma\Pi$ values determined for different aqueous-solutions (at stoichiometric saturation with respect to a same given solid-composition) varied as a function of aqueous-solution composition. An examination of Walter and Morse's experimental findings shows, however, that $\Sigma\Pi_{ss}$ values varied *predictably* as a function of aqueous-solution composition (see app. and table 1).
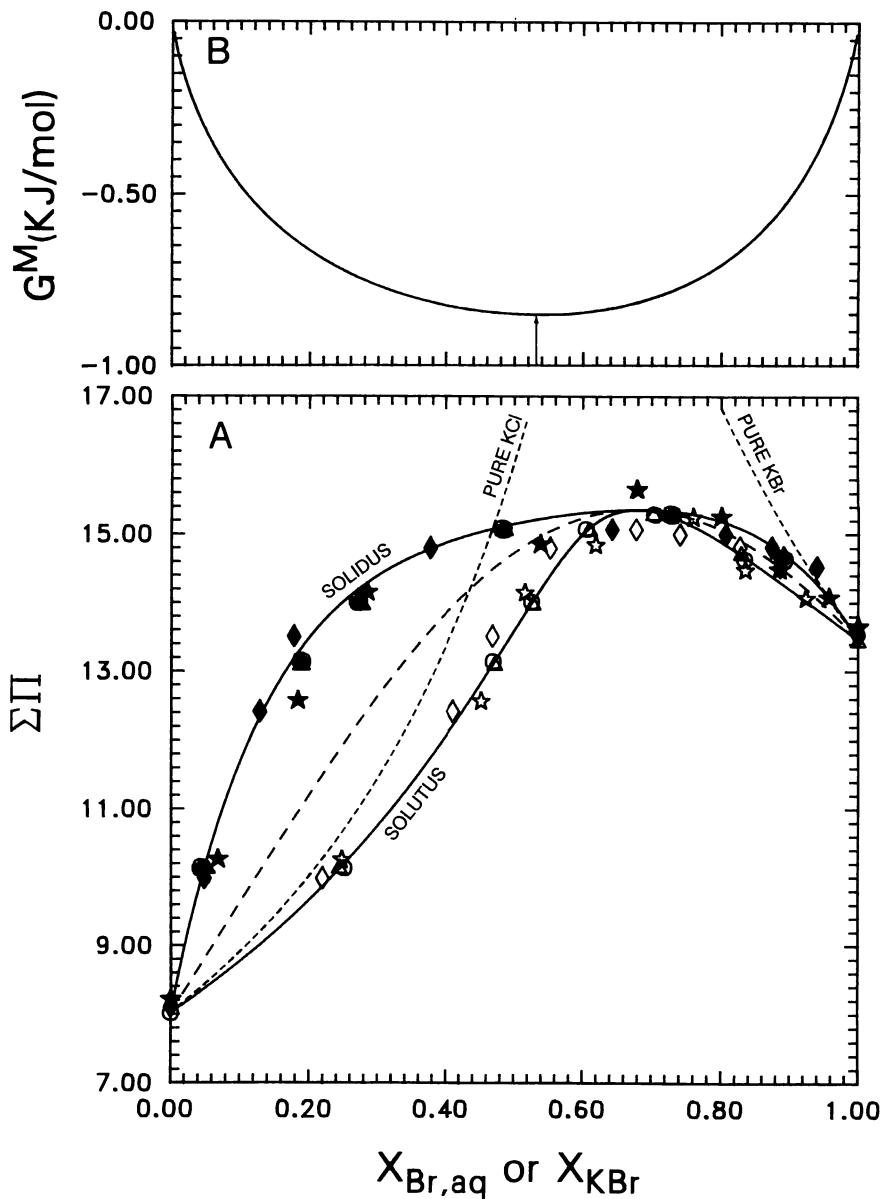
Fig. 6. Lippmann phase diagram for the K(Cl, Br)–H₂O system at 25°C showing the results of Amadori and Pampani (1911, lozenges), Flatt and Burkhardt (1944, stars), and Durham and others (1953, circles and triangles). Open symbols indicate aqueous-solution compositions. Filled-in symbols indicate solid-phase compositions. Circles indicate Durham and others's set of experiments with initial KCl solids; triangles give the results of their set of experiments with initial KBr solids. All aqueous ion activities were determined using the PHRQPITZ aqueous-speciation model of Plummer and others (1988). The Lippmann solidus and solutus curves are drawn from a least-squares fit of Durham and others' results to a Guggenheim two-parameter sub-regular model ($a_0 = 1.40$, $a_1 = -0.08$). Endmember pK's are -0.904 for KCl and -1.129 for KBr (Durham and others, 1953). The long-dashed curve shows the fitted "minimum stoichiometric saturation" line for the system. The line joins the solidus and solutus curves at an alyotropic maximum located at ($\chi_{Br} = 0.676$, $\Sigma\Pi = 15.35$). (B) Gibbs free energy of mixing curve for the K(Cl, Br)–H₂O system. The arrow points to the minimum in the G^M curve.

TABLE 1

Interpretation of the stoichiometric saturation states determined by Walter and Morse (1984) from four magnesian calcite dissolution experiments

Solid composition (mole % Mg):	12%	12%	18%	18%
Aqueous Mg^{2+}/Ca^{2+} ratio:	1/5	5/1	1/5	5/1
$p\Sigma\Pi$ reported by Walter and Morse (1984):	8.11	7.56	7.73	7.30
pK_{ss} reported by Walter and Morse (1984):	8.28	8.27	7.94	7.95
pK_{ss} calculated using eq (56) and Walter and Morse's $p\Sigma\Pi$ values:	8.27	8.25	7.93	7.95

STOICHIOMETRIC SATURATION VERSUS THERMODYNAMIC EQUILIBRIUM CONTROLS IN LOW TEMPERATURE SSAS SYSTEMS

Walter and Morse's (1984) experiments (discussed in app.) support the concept of stoichiometric saturation as a dissolution-controlling thermodynamic state which can be attained in the $(Ca, Mg)CO_3–H_2O$ system or at the least as one that can be determined by extrapolation. Gamsjäger (1985) observed that $(Co, Mn)CO_3$ solid-solutions dissolved congruently in aqueous acidic media at $50°C$, and that the composition of the solids remained constant in all cases. Gamsjäger concluded that his aqueous solutions had attained "a steady state characterized by equal G-functions of the solid and solute species rather than equal chemical potentials of the endmember carbonates in the phases present." Plummer and Busenberg's (1987) experiments on $(Sr, Ca)CO_{3orth.}$ offer perhaps the best evidence supporting stoichiometric saturation as a state that can be attained during solid-solution dissolution experiments. As discussed previously, a solutus curve can never lie above the pure endmember saturation curves in a Lippmann phase diagram. Plummer and Busenberg's highly reproducible congruent-dissolution results generally lie well above the solutus and pure phase curves. Attainment of thermodynamic equilibrium or primary saturation states, therefore, can not explain their results, at $25°$ or at $76°C$ (figs. 7, 8). The solutus and the dashed curve displaying the family of "minimum stoichiometric saturation" points at $76°C$ near the aragonite endmember are close together; consequently it can not be completely excluded that the $76°C$ experimental results in this particular region may represent thermodynamic equilibrium or primary saturation. As discussed further in Glynn and others (1990), the assumption that Plummer and Busenberg's (1987) experimental results lie very close to actual stoichiometric saturation states is consistent with the miscibility gap observed in the distribution of natural low-temperature hydrothermal $(Sr, Ca)CO_3$ solids. Higher stoichiometric solubilities would predict a greater miscibility gap than observed in these minerals.

There is currently little evidence that stoichiometric saturation states may control solid-solution precipitation processes. Stoessell and Carpenter (1986) suggest that stoichiometric saturation does control the initial partitioning of trace bromide during $Na(Cl, Br)$ and $K(Cl, Br)$ precipitation. The NaBr and KBr solid-phase activity-coefficients deter-
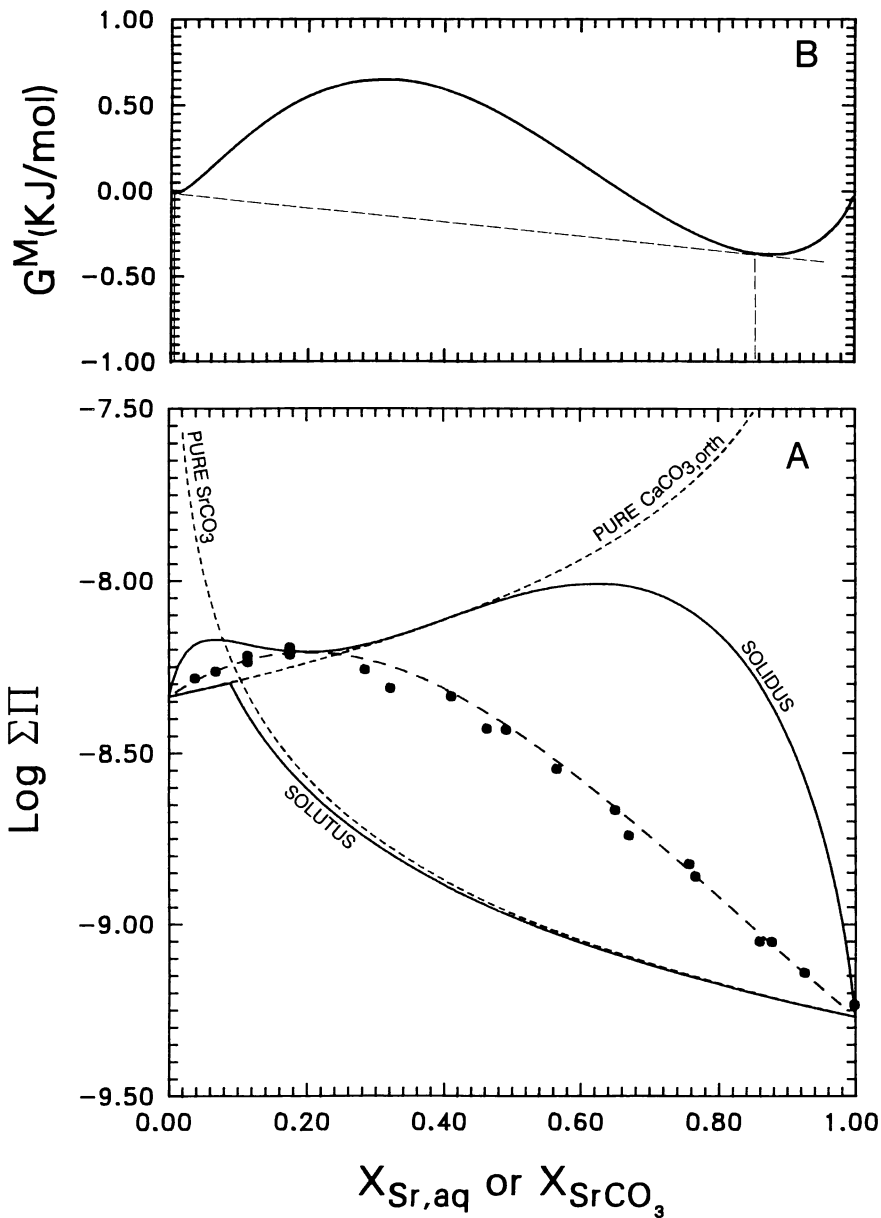
Fig. 7(A) Lippmann phase diagram for the $(Ca, Sr)CO_{3orth}-H_2O$ system at $25°C$ constructed using the congruent dissolution data (plotted points) of Plummer and Busenberg (1987) and their fitted values to the Guggenheim (1937) sub-regular excess-free-energy model ($a_0 = 3.43$, $a_1 = -1.82$). The long-dashed curve is the "minimum stoichiometric saturation" curve, calculated using Plummer and Busenberg's fitted a_0 and a_1 values and endmember pK's of 8.336 for aragonite (Plummer and Busenberg, 1982) and 9.271 for strontianite (Busenberg, Plummer, and Parker, 1984). (B) Gibbs free energy of mixing curve for the $(Ca, Sr)CO_{3orth}-H_2O$ system at $25°C$. The dashed lines represent the miscibility gap determined from the common-tangent points of the G^M curve. The miscibility gap could also be determined from the Lippmann diagram by finding the intersections of the solidus curve with a straight horizontal through the "eutectic" point on the solutus curve. The spinodal compositions (inflexion points on the G^M curve) correspond to the two maxima in the solidus curve.
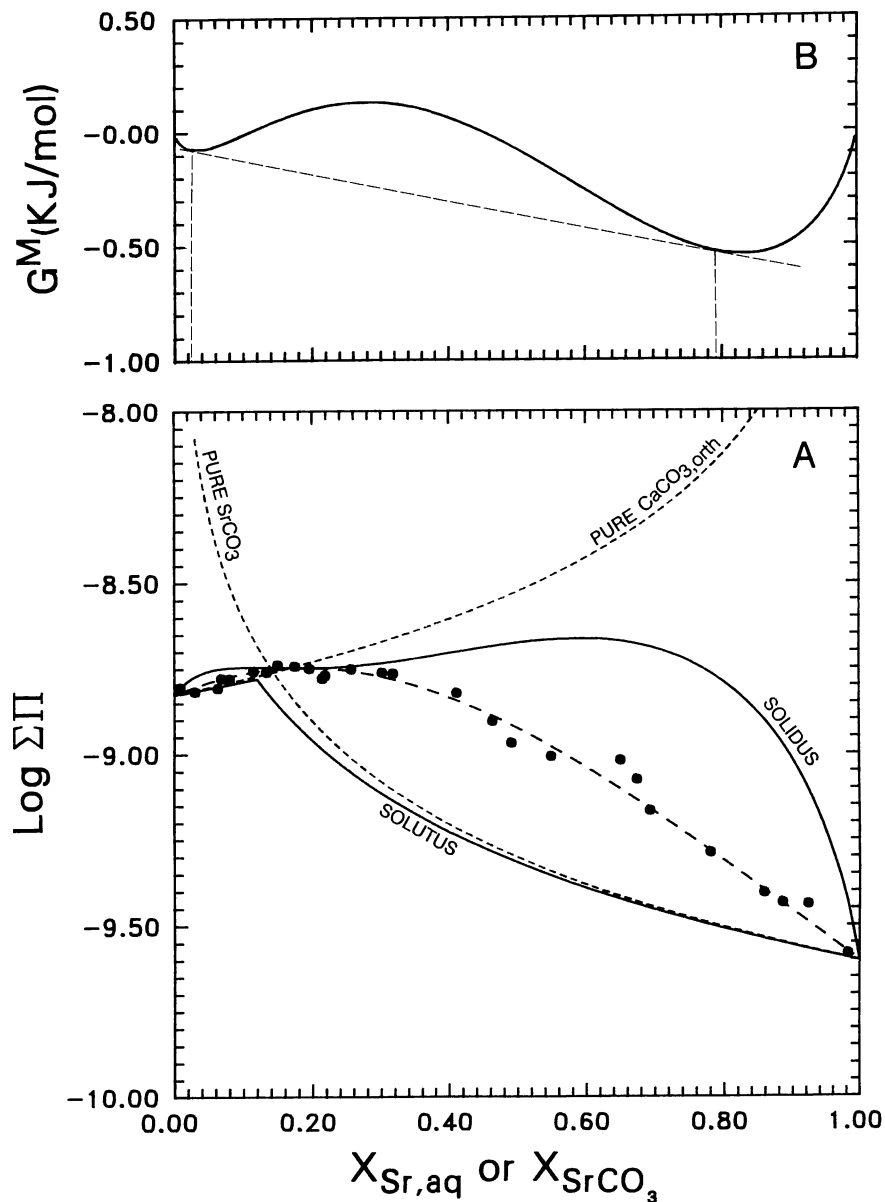
Fig. 8(A) Lippmann phase diagram for the (Ca, Sr)CO$_{3orth}$–H$_2$O system at 76°C constructed using the congruent dissolution data (plotted points) of Plummer and Busenberg (1987) and their fitted values to the Guggenheim (1937) sub-regular excess-free-energy model (a$_0$ = 2.66, a$_1$ = −1.15). The long-dashed curve is the "minimum stoichiometric saturation" curve, calculated using Plummer and Busenberg's fitted a$_0$ and a$_1$ values and endmember pK's of 8.826 for aragonite (Plummer and Busenberg, 1982) and 9.604 for strontianite (Busenberg, Plummer, and Parker, 1984). (B) Gibbs free energy of mixing curve for the (Ca, Sr)CO$_{3,orth}$–H$_2$O system at 76°C. The dashed lines represent the miscibility gap determined from the common-tangent points of the G^M curve.

mined by Stoessell and Carpenter, using the assumption of stoichiometric saturation, are not consistent however with the theory that the energy (and therefore the activity coefficient) of the Br ion should be smaller in the KCl lattice than in the NaCl lattice. This concept is reviewed by Kirgintsev and Trushnikova (1966) and Urusov (1974). Stoessell and Carpenter's activity coefficients also differ from the values that can be determined (Kirgintsev and Trushnikova, 1966; Glynn and others, 1990) from the thermodynamic equilibrium data of Durham and others (1953) and Simons and others (1952) for the K(Cl, Br)–H$_2$O and Na(Cl, Br)–H$_2$O systems. The applicability of the stoichiometric saturation concept to solid-solution precipitation processes is further discussed by Glynn and others (1990).

The evidence that stoichiometric saturation controls dissolution processes for some solid-solution systems does not imply that thermodynamic equilibrium can never be attained in laboratory dissolution experiments on other systems or under other conditions. Durham and others (1953) give convincing evidence for the attainment of thermodynamic equilibrium during recrystallization experiments in the K(Cl, Br)–H$_2$O, Rb(Cl, Br)–H$_2$O, and (K, Rb)Br–H$_2$O systems. The experiments consisted in placing a pure endmember solid-phase in an aqueous solution of the opposite endmember component. In a second set of experiments the solid-phase and aqueous-phase endmembers were reversed, the relative amounts of solid and aqueous phase adjusted to match the total compositions of the first experimental set. After three to four weeks, Durham and others (1953) found that each matched pair of experiments had produced identical solid-solution compositions (to within 1 percent of each other). Final aqueous-solution compositions were also identical in each matched pair. To achieve this result for an array of total aqueous-phase solid-phase compositions, from opposite initial conditions, indicates that thermodynamic equilibrium can indeed be achieved at low temperatures in SSAS systems with highly soluble salts. Using a similar technique to Durham and others (1953), Simons and others (1952) also demonstrated the attainment of thermodynamic equilibrium during recrystallization experiments in the Na(Cl, Br)–NaOH–H$_2$O system.

The fairly good agreement between the K(Cl, Br) recrystallization results of Durham and others (1953) and those of Flatt and Burkhardt (1944) and Amadori and Pampani (1911) offers further evidence that thermodynamic equilibrium was attained in these three studies. The K(Cl, Br)–H$_2$O experimental results were reinterpreted with the help of the PHRQPITZ mass-transfer and aqueous-speciation model (Plummer and others 1988). Guggenheim a_0 and a_1 parameters were determined from a least squares fit of the K_{ss} constants calculated from Durham and others's (1953) data. Figure 6 shows the various experimental results together with the fitted Lippmann solidus and solutus curves. The "minimum stoichiometric saturation" curve is also shown. This curve gives approximately the aqueous-solution compositions that would be obtained if K(Cl, Br) solid-solutions could dissolve congruently to stoi-

chiometric saturation in initially pure water (the assumption made is that the ratio of the total aqueous concentrations of Br and Cl can be considered equal to the aqueous activity ratio of Br^- and Cl^-).

A characteristic feature of the "minimum stoichiometric saturation" curve is its downward concavity when displayed on a Lippmann diagram. This feature occurs in ideal SSAS systems as well as in systems with miscibility gaps or alyotropic extrema. (In the special case of an alyotropic minimum, the curve can be seen as two downwardly concave segments). The final aqueous-solution compositions determined from the experiments of Durham and others (1953), Flatt and Burkhardt (1944), and Amadori and Pampani (1911) do not show this characteristic shape of "minimum stoichiometric saturation" states. The (Sr, Ca) CO_{3orth} dissolution results of Plummer and Busenberg (1987), however, do show this characteristic feature.

The best available experimental results indicate that whereas stoichiometric saturation must be invoked to explain dissolution results for relatively insoluble solid-solutions such as magnesian-calcites, cobalt-rhodochrosites, and strontian-aragonites, thermodynamic equilibrium (which is also a stoichiometric saturation state) can nonetheless be achieved at low-temperatures in highly soluble solid-solution systems, such as $K(Cl, Br)-H_2O$, $Rb(Cl, Br)-H_2O$, $(K, Rb)Br-H_2O$, and $Na(Cl, Br)-H_2O$.

Lippmann phase diagrams and the concept of stoichiometric saturation can also be used to describe SSAS systems at high temperatures and pressures. Because recrystallization rates will typically be much faster than at low temperatures, the concept of stoichiometric saturation may not be as important in interpreting SSAS experimental data. The inaccuracies involved in estimating the thermodynamic properties and compositional details of the aqueous phase will present the major difficulty in the interpretation of experimental results in such systems.

CONCLUSIONS

1. The Thorstenson and Plummer (1977) stoichiometric saturation model is reviewed, and a new derivation of the relation between solid-phase component activities and K_{ss} stoichiometric saturation constants is presented. In this derivation, Thorstenson and Plummer's standard chemical potential μ_{ss}^0 for the one component solid $B_{1-x}C_xA$ is equated to the molar free energy of the *binary* solid-solution and therefore to the compositionally-weighted average of the endmember chemical potentials (μ_{BA} and μ_{CA}). Using this approach, the excess free energy of mixing (G^E) of a $B_{1-x}C_xA$ solid-solution can be determined algebraically from the stoichiometric saturation constant K_{ss}, the endmember solubility products K_{BA} and K_{CA}, and the composition of the solid.

2. Experimentally-determined G^E values can be fitted, thereby defining the thermodynamic properties of a solid-solution series on the basis of the endmember stabilities and one or two adjustable parameters (such as a_0 and a_1 in eq 35). This approach, while requiring an appropri-

ate G^E function, avoids Thorstenson and Plummer's (1977) technique of determining solid-phase activity-coefficients by relating them to the derivative $\partial K_{ss}/\partial x$ at every composition x.

3. The Lippmann (1977, 1980) "total-solubility-product" model is examined. A general formulation of Lippmann's solutus equation is presented, applicable for non-ideal solid-solutions. The minimum solubility concept of "primary saturation" is related to Lippmann's solidus and solutus curves and to thermodynamic equilibrium. An equation relating Thorstenson and Plummer's (1977) IAP_{ss} variable to Lippmann's (1977) $\Sigma\Pi$ variable is developed. This relation allows the representation of stoichiometric saturation curves on Lippmann diagrams and leads to a better understanding of the concept of stoichiometric saturation and its relation to thermodynamic equilibrium and "primary saturation" states. Similarly, Lippmann phase diagrams can be used to represent endmember saturation curves, which may then be compared to the minimum solubility states represented by Lippmann's solutus curve.

4. The best available experimental results indicate that stoichiometric saturation states can be achieved during the dissolution of relatively insoluble solids (Walter and Morse, 1984; Plummer and Busenberg, 1987; Gamsjäger, 1985). On the other hand, the alkalihalide recrystallization experiments of Durham and others (1953), Simons and others (1952), Flatt and Burkhardt (1944), and Amadori and Pampani (1911) demonstrate that thermodynamic equilibrium can be obtained after three to four weeks at $25°C$ in systems with highly soluble solid-solutions.

APPENDIX

Lafon's criticisms of the stoichiometric saturation concept.—Lafon (1978) admitted that determining the stoichiometric saturation state of a solid-solution is "one of the more useful methods" for determining its free energy. Lafon nevertheless questioned the applicability of Thorstenson and Plummer's model to general geochemical reactions, stating that "there are no well-known, practical mechanisms in nature for selecting a particular composition a priori and maintaining it fixed." Lafon therefore argued that while stoichiometric saturation may apply to congruent dissolution reactions, stoichiometric saturation should not be used as a model describing precipitation or recrystallization

reactions, for which it is difficult to determine in advance the final solid-phase composition because:

1. Initial or earlier-produced phases are not likely to maintain a fixed composition.
2. Kinetic factors play an important role in determining the composition of solid solutions formed during precipitation and recrystallization processes.

Lafon (1978) also criticized the laboratory technique (from Plummer and Mackenzie, 1974) used by Thorstenson and Plummer to determine stoichiometric saturation constants for the magnesian calcite series. The technique specifically consisted in extrapolating pH values obtained during the congruent dissolution of a magnesian calcite to infinite time by plotting the data against an inverse square root of time axis, and determining the intercept. This technique, however, has since been abandoned by Plummer (personal commun., 1986) and Plummer and Busenberg (1987). Other researchers (Bischoff and others, 1987; Walter and Morse, 1984; Mackenzie and others, 1983) have continued using this technique and claim that it does give reproducible results.

Lafon's criticisms seem valid, inasmuch as the concept of stoichiometric saturation has so far not been conclusively demonstrated to apply to solid-solution precipitation processes (Glynn and others, 1990). However, as can be seen from the experiments of Walter and Morse (1984) and Plummer and Busenberg (1987), Lafon's criticisms do not undermine the validity of stoichiometric saturation as a theoretically and experimentally useful concept which can help in the interpretation and prediction of SSAS dissolution processes (see discussion in the text).

Gresens' hypothetical test of the Thorstenson and Plummer model.—Gresens (1981a, b) gave support to the Lippmann model's formulation of the total solubility product and criticized Thorstenson and Plummer's use of fractional exponents in the stoichiometric saturation expression. While objecting to the Thorstenson and Plummer formulation, Gresens accepted the concept of stoichiometric saturation and claimed that Lippmann's total solubility product ($\Sigma\Pi = [A^-] ([B^+] + [C^+])$) could be used not only to describe thermodynamic equilibrium but also stoichiometric saturation.

In his first argument against the Thorstenson and Plummer expression for K_{ss} Gresens (1981a) developed the following thought experiment:

"Consider a solid-solution aqueous-solution (SSAS) system where the aqueous mass is very small and the solid mass infinitely large. Assume that the solid has a very low solubility and a chemical composition consistent with its chemical formula, $B_{.5}C_{.5}A$. The solid is brought into contact with the aqueous phase. Initially, the solid dissolves stoichiometrically, until a state of stoichiometric saturation is reached. The solid and the solution then continue reacting toward thermodynamic equilibrium by ion for ion exchange of B and C."

At stoichiometric saturation, the Thorstenson and Plummer model gives an ion activity product (IAP_{ss}) equal to:

$$IAP_{ss} = [B^+]^{0.5}[C^+]^{0.5}[A^-] \tag{A1}$$

Because $[B^+] \simeq [C^+]$ (assuming no difference in their activity coefficients or ion-pairing propensities), eq (A1) can be reduced to:

$$IAP_{ss} = [B^+][A^-] \tag{A2}$$

After an increment of exchange i (of B for C), the IAP expression becomes:

$$IAP_{ss}^* = ([B^+] + i)^{0.5} ([C^+] - i)^{0.5} [A^-] \tag{A3}$$

which is equivalent to:

$$IAP_{ss}^* = ([B^+]^2 - i^2)^{0.5} [A^-] \tag{A4}$$

Thus, the new ion activity product IAP_{ss}^* will always be smaller than the original ion activity product IAP_{ss} at stoichiometric saturation, no matter which direction of exchange of B^+ for C^+ is chosen. From this observation, Gresens (1981a) reasoned that because K_{ss} was constant under the conditions of the thought experiment, the solution would always become undersaturated after an increment of exchange. In other words, once stoichiometric saturation was reached, the initial increment of exchange would always proceed as if the original state of stoichiometric saturation was always the state of minimum solubility. Gresens concluded that such behavior was "obviously not true" and was an "artifact of the formulation of the saturation statement as a solubility product that employs fractional exponents."

Although Gresens' argument appears compelling, it is predicated on the assumption that once stoichiometric saturation is reached, evolution toward thermodynamic equilibrium will occur only by ion for ion exchange of the two substituting ions, without any further net dissolution or precipitation. In other words, Gresens assumes that the aqueous activity $[A^-]$ of the non-substituting ion remains constant. In fact, if after an increment of exchange the aqueous-solution is still at stoichiometric saturation (with respect to $B_{1-x}C_xA$), the aqueous activity of the non-substituting ion A^- (and therefore the solubility of the solid) *must* necessarily be greater than that of a system at "minimum stoichiometric saturation." This principle is a direct result of considering the solid $B_{1-x}C_xA$ as a pure phase and does not reflect on some mathematical inadequacy of the K_{ss} notation in representing stoichiometric saturation.

Consider a pure solid phase BA initially at thermodynamic equilibrium with an aqueous phase containing A^- and B^+ ions. If after some process (cation exchange for example) the activity of B^+ in the aqueous phase is decreased and if somehow this decrease is maintained, the activity of A^- in solution will increase to compensate for the decrease in $[B^+]$. Consequently, the solubility of the solid can be said to be greater than it was in the initial system. This is a direct result of the law of mass action as applied to a pure solid BA. The same principle occurs in a SSAS system at stoichiometric saturation with respect to a phase $B_{1-x}C_xA$. The whole concept of stoichiometric saturation, as defined by Thorstenson and Plummer (1977), impinges on the assumption that under certain conditions, a solid-solution can be considered to behave with an invariant composition, that is, as a pure phase. Therefore considering Gresen's thought experiment, if for some reason an exchange of B^+ for C^+ occurs in the aqueous solution, without significantly affecting the free energy of the initial solid (of which there is an infinite amount), the aqueous activity of A^- should increase regardless of the direction of exchange if the aqueous phase is to remain at stoichiometric saturation with respect to the initial solid.

Let us consider this point mathematically. At "minimum stoichiometric saturation", the aqueous phase is defined by:

$$IAP_{ss} = [B^+]^{1-x}[C^+]^x [A^-] = K_{ss} \tag{A5}$$

After an increment i of exchange (possibly accompanied by dissolution/precipitation), a new ion activity product can be defined:

$$IAP_{ss}^* = ([B^+]_*)^{1-x}([C^+]_*)^x[A^-]_* \tag{A6}$$

By the definition of stoichiometric saturation, both the initial solution and the solution present after an increment of exchange will be at stoichiometric saturation with respect to the initial solid $B_{1-x}C_xA$ if:

$$IAP_{ss} = IAP_{ss}^* = K_{ss} \tag{A7}$$

which is equivalent to:

$$\frac{[A^-]_*}{[A^-]} = \frac{[B^+]^{1-x}[C^+]^x}{[B^+]_*^{1-x}[C^+]_*^x} \tag{A8}$$

Assuming a closed system with no aqueous ion pairing and with equal aqueous activity coefficients, the following relations will apply:

$$[A^-] = [B^+] + [C^+] \tag{A9}$$

and

$$[A^-]_* = [B^+]_* + [C^+]_* \tag{A10}$$

If the activity fractions $\chi_{B,aq}$ and $\chi_{C,aq}$ are defined as in eqs (41) and (42) and if $\chi^*_{B,aq}$ and $\chi^*_{C,aq}$ are similarly defined, eq (A8) can be transformed to:

$$\frac{[A^-]_*}{[A^-]} = \frac{(\chi_{B,aq}[A^-])^{1-x}(\chi_{C,aq}[A^-])^x}{(\chi^*_{B,aq}[A^-]_*)^{1-x}(\chi^*_{C,aq}[A^-]_*)^x} \tag{A11}$$

which is equivalent to:

$$\frac{[A^-]^2_*}{[A^-]^2} = \frac{(\chi_{B,aq})^{1-x}(\chi_{C,aq})^x}{(\chi^*_{B,aq})^{1-x}(\chi^*_{C,aq})^x} \tag{A12}$$

which, by virtue of the conditions of Gresens' thought experiment, is equivalent to:

$$\frac{[A^-]^2_*}{[A^-]^2} = \frac{(1-x)^{1-x}x^x}{(1-\chi^*_{C,aq})^{1-x}(\chi^*_{C,aq})^x} \tag{A13}$$

Eq (A13) demonstrates that the activity of the non-substituting ion A^- in an aqueous-solution at "minimum stoichiometric saturation" (for which $\chi^*_{C,aq} = x$) with respect to $B_{1-x}C_xA$ will always be smaller than the activity of A^- in a solution which is not at "minimum stoichiometric saturation", the reason being that the denominator term $(1 - \chi^*_{C,aq})^{1-x}(\chi^*_{C,aq})^x$ has a maximum value when $\chi^*_{C,aq} = x$.

Consequently, once stoichiometric saturation is reached, evolution of the system to final thermodynamic equilibrium cannot occur only by simple ion for ion exchange, as Gresens suggests, but must also be accompanied by a net dissolution of the solid. This is true as long as the solution maintains itself at stoichiometric saturation with respect to $B_{1-x}C_xA$ throughout its evolution toward thermodynamic equilibrium.

Gresens' second criticism of the Thorstenson and Plummer model.—The thermodynamic principles predicting the behavior of SSAS systems can be applied regardless of whether the solid is composed of chemically different or isotopically different substituting ions. In fact, the ratio of the solubility products of two chemically similar but isotopically different solid-phases is directly related to the fractionation factor expressing isotopic equilibrium between a solid phase and an aqueous solution. The thermodynamic properties of solid-solutions are generally dependent on the differences in mass, ionic radius, electronic charge, and polarizability of the substituting ions. In comparison, the free energy of mixing of an isotopic solid-solution will depend almost exclusively on the difference in mass between the two substituting isotopes. This difference in mass will cause compounds of different isotopes to have different thermodynamic properties, even though the differences may often be too small to measure. Gresens (1981a) argued that conventional solubility product expressions for chemically pure compounds are not written as a product series of individual isotopic components raised to their mole fraction. For example, applying Thorstenson and Plummer's (1977) stoichiometric saturation notation to the case of a calcite containing two calcium isotopes gives the following equation:

$$a_{CaCO_3}K^{calcite}_{ss} = [^{40}Ca^{2+}]^{0.98}[^{44}Ca^{2+}]^{0.02}[CO_3^{2-}] \tag{A14}$$

where the fractional exponents represent the relative natural abundances of the calcium isotopes.

In practice, the common solubility product expression for calcite, inherently assumes that the calcium ion activity is the sum of all the calcium isotope activities:

$$[Ca^{2+}] = ([^{40}Ca^{2+}] + [^{44}Ca^{2+}]) \qquad (A15)$$

While Gresens' statement on the implicit handling of isotope activities in conventional solubility products is correct, it can nevertheless be shown (demonstration in Denis, 1981) that it is only a matter of convention, considering that the K_{ss} notation does have all the properties required to describe not only stoichiometric saturation but also thermodynamic equilibrium.

Indeed, for a given calcite isotopic composition and given aqueous activities of ^{40}Ca and ^{44}Ca at "minimum stoichiometric saturation," the term $[^{40}Ca^{2+}]^{0.98}[^{44}Ca^{2+}]^{0.02}$ is as much a constant as the term $([^{40}Ca^{2+}] + [^{44}Ca^{2+}])$. The important property of either expression is that if the activity of the non-substituting ion CO_3^{2-} should change, say decrease by 10 percent, the terms $[^{40}Ca^{2+}]^{0.98}[^{44}Ca^{2+}]^{0.02}$ or $([^{40}Ca^{2+}] + [^{44}Ca^{2+}])$ should correspondingly change (increase by 10 percent to compensate and maintain a constant solubility product). In both formulations, this can be done by increasing the individual ion activities of ^{40}Ca and ^{44}Ca by 10 percent.

An advantage of using the K_{ss} notation to predict stoichiometric saturation states is that regardless of the congruency of the solution, Thorstenson and Plummer's ionic activity product IAP_{ss} will always be constant and equal to K_{ss} as long as the aqueous solution is at stoichiometric saturation with respect to the given solid $B_{1-x}C_xA$. The same cannot be said of Lippmann's $\Sigma\Pi$ formulation where the activities of the substituting ions are added together.

Denis (1982) also reviewed Gresens' two arguments against Thorstenson and Plummer's K_{ss} formulation. His criticisms of Gresens' arguments are similar to ours: (1) evolution from a state of stoichiometric saturation to a state of thermodynamic equilibrium (with respect to the solid present at stoichiometric saturation) can only occur by a further dissolution of the solid and not solely by ion for ion exchange as Gresens suggests; (2) the K_{ss} formulation when applied to an isotope solid-solution does yield a constant solubility product (for a given isotopic solid composition) and thus obeys the conventional solubility product rule.

Lippmann's criticisms on the use of fractional exponents in solubility product expressions. — Lippmann (1977) criticizes the use of fractional exponents in solubility product expressions for solid-solutions. In support of his argument, Lippmann reasons that the law of mass action assumes chemical purity of reactants and products, thereby implying that compounds form according to the law of definite proportions. According to this law, stoichiometric coefficients must be small integers. Indeed, non-fractional coefficients are evident in mass action expressions for the formation of molecular compounds. In a similar guise, the electroneutrality condition requires non-fractional exponents in the solubility product expression for complex ionic crystals: stoichiometric coefficients are directly derived from valence numbers, which are always integer numbers.

Lippmann (1977) furthers his argument, stating that at ordinary temperatures most crystalline minerals contain non-fractional multiples of their chemical formulae in their unit cells, because equipoints are either completely filled or completely vacant, and equipoints represent whole number multiples of atomic sites per unit cell (equipoints are sets of atomic sites compatible with space-group symmetry). According to Lippmann (1977), "fractional occupation of one or more equipoints would be equivalent to variable composition and would exclude a mineral from the normal solubility product approach . . . invariant composition, as it is required for the solubility product to be valid, implies complete and homogeneous occupation of certain equipoints and (commonly) complete vacancy of others. Because equipoints are characterized by whole number multiplicity

according to space group theory, only minerals with non-fractional subscripts in their formulae are hopeful candidates for applications of the solubility product."

Lippmann's criticism seems more a matter of convention than a criticism on the fundamental validity of the K_{ss} notation. In particular, the idea that stoichiometric coefficients must be small integers seems rather arbitrary.

Walter and Morse's test of the Lippmann model.—Walter and Morse (1984) used the results of dissolution experiments on 12 and 18 percent magnesian calcites (of marine origin) to argue against the Lippmann $\Sigma\Pi$ formulation. The experiments consisted of equilibrating the two magnesian calcites with two different $MgCl_2$–$CaCl_2$–H_2O solutions, one with a 5 to 1 Mg to Ca ratio and the other with a 1 to 5 ratio. The magnesium and calcium concentrations of the solution being fixed (by their high initial concentrations), carbonate activities were determined at stoichiometric saturation using Plummer and Mackenzie's (1974) technique of extrapolating pH against the inverse square root of time.

Walter and Morse observed that their experimentally-determined Ca^{2+}, Mg^{2+}, and CO_3^{2-} equilibrium activities gave rise to the same K_{ss} values for a given magnesian calcite composition, irrespective of the aqueous Mg^{2+}/Ca^{2+} ratio. In contrast, their calculated $\Sigma\Pi$ values were not constant. Walter and Morse therefore argued that the Lippmann model failed "to accurately represent a consistent equilibrium constant value at stoichiometric saturation in different solutions."

Although Walter and Morse's experiments do support their claim that their kinetically extrapolated K_{ss} values represent stoichiometric saturation states, this observation does not invalidate the Lippmann model and should not necessarily deter the use of the $\Sigma\Pi$ variable in assessing the thermodynamic state of a SSAS system. Indeed, Lippmann did not claim that $\Sigma\Pi$ could be used as a descriptor of stoichiometric saturation. In its original design, the Lippmann model focused only on thermodynamic equilibrium. As demonstrated earlier, the value of the $\Sigma\Pi$ variable will, at stoichiometric saturation with respect to a phase $B_{1-x}C_xA$, be dependent on the $[C^+]/[B^+]$ ratio of the solution. This fact does not necessarily invalidate the use of $\Sigma\Pi$ as a measure of stoichiometric saturation. As can be seen from table 1, the K_{ss} values, which can be calculated (using eq 56) from the $\Sigma\Pi$ values determined by Walter and Morse, are essentially identical to their reported K_{ss} values. Therefore, Lippmann's $\Sigma\Pi$ notation combined with eq (56) can be used to predict stoichiometric saturation states.

REFERENCES

Amadori, M., and Pampani, G., 1911, Sulla capacita degli alogenuri potassici di dare soluzioni solide, in rapporto collar temperatura: Atti della Reale dei Licei, series 5 (classe di scienze fisiche, mathematiche e naturali), v. 20, p. 473–480.

Berndt, A. F., and Stearns, R. I., 1973, The equilibrium between a solid solution and an aqueous solution of its ions: Journal of Chemical Education, v. 50, no. 6, p. 415–417.

Berner, R. A., 1975, The role of magnesium in the crystal growth of calcite and aragonite from sea water: Geochimica et Cosmochimica Acta, v. 39, p. 489–504.

Berry, R. S., Rice, S. A., and Ross, J., 1980, Physical Chemistry: New York, John Wiley & Sons, 1264 p.

Berthelot, M., 1872, On the law which governs the distribution of a substance between two solvents: Annales de Chimie et de Physique, fourth series, v. 26, p. 408–417.

Bischoff, W. D., Mackenzie, F. T., and Bishop F. C., 1987, Stabilities of synthetic magnesian calcites in aqueous solutions: Comparison with biogenic materials: Geochimica et Cosmochimica Acta, v. 51, p. 1413–1423.

Braitsch, O., 1971, Salt Deposits. Their Origin and Composition: Berlin, Springer Verlag, 297 p.

Busenberg, E., Plummer, L. N. and Parker, V. B., 1984, The solubility of strontianite ($SrCO_3$) in CO_2–H_2O solutions between 2 and 91°C, the association constants of $SrHCO_3^+$(aq) and $SrCO_3^0$(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr^{2+}(aq) and $SrCO_3$(cr) at 25°C and 1 atm total pressure: Geochimica et Cosmochimica Acta, v. 48, p. 2021–2035.

Carlson, H. C., and Colburn, A. P., 1942, Vapour-liquid equilibria of non-ideal solutions: Industrial and Engineering Chemistry v. 34, p. 581–589.

Crocket, J. H., and Winchester, J. W., 1966, Coprecipitation of zinc with calcium carbonate: Geochimica et Cosmochimica Acta, v. 30, p. 1093–1109.

Dandurand, J. L., and Schott, J., 1980, Remarques sur les conditions d'application de la loi d'action de masse à la determination des parametrès thermodynamiques des mineraux à basse temperature: Bulletin de Mineralogie, v. 103, p. 307–316.

Davies, C. W., 1962, Ion Association: London, Butterworth & Co. 190 p.

Davis, J. A., Fuller, C. C., and Cook, A. D., 1987, A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation: Geochimica et Cosmochimica Acta, v. 51, p. 1477–1490.

Debye, P., and Hückel, E., 1923, The theory of electrolytes. I. Lowering of freezing point and related phenomena: Physikalische Zeitschrift, v. 24, p. 185.

Deer, W. H., Howie, R. A., and Zussmann, J., 1963, Rock-Forming Minerals, 5 volumes: London Longmans.

Delaney, C. M., and Nash, L. K., 1977, On mole fractions in equilibrium constants: Journal of Chemical Education, v. 54, no. 3, 151–153.

Denbigh, K., 1981, The Principles of Chemical Equilibrium, 4th ed.: Cambridge, U.K., Cambridge University Press, 494 p.

Denis, J., ms, 1982, Comportement des Elements Tràces lors de la Dissolution des Mineraux — Application aux Sources des Alpes: Doctorat de Specialité, Université Paris VII, 87 p.

Denis, J., and Michard, G., 1983, Dissolution d'une solution solide: étude theorique et experimentale: Bulletin de Mineralogie, v. 106, p. 309–319.

Durham, G. S., Rock, E. J., and Frayn, S. F., 1953, Solid solutions of the alkali halides. I. The systems $KBr-KCl-H_2O$, $RbBr-RbCl-H_2O$, $RbBr-KBr-H_2O$ at 25°: Journal of the American Chemical Society, v. 75, p. 5793–5794.

Doerner, H. A., and Hoskins, W. M., 1925, Coprecipitation of radium and barium sulfates: Journal of the American Chemical Society, v. 47, p. 662–675.

Flatt, R., and Burkhardt, G., 1944, Untersuchungen über Mischkrystallbildung in Lösungen. II. Die Systeme $KCl + NH_4Cl + H_2O$, $KBr + NH_4Br + H_2O$, $KCl + KBr + H_2O$ und $NH_4CL + NH_4Br + H_2O$ bei 25°: Helvetica Chimica Acta, v. 27, p. 1605–1610.

Gamsjäger, H., 1985, Solid state chemical model for the solubility behaviour of homogeneous solid Co-Mn-carbonate mixtures: Berichte Bunsengesellschaft für Physikalische Chemie, v. 89, p. 1318–1322.

Garrels, R. M., and Christ, C. L., 1965, Solutions, Minerals, and Equilibria, 2d. ed.: New York Harper and Row, 450 p.

Garrels, R. M., and Wollast, R., 1978, Discussion of: "Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase. Example: the magnesian calcites": American Journal of Science, v. 278, p. 1469–1474.

Glynn, P. D., 1989a, Modeling solid-solution reactions in low-temperature aqueous systems, *in* Melchior, D. C., Bassett, R. L., eds., Modeling in Aqueous Systems II: American Chemical Society Symposium Series, v. 416, p. 74–86.

———— 1989b, MBSSAS: A computer code for the Margules parametrization of equilibrium relations in binary solid-solution aqueous-solution systems: submitted to Computers in Geosciences.

Glynn, P. D., Reardon, E. J., Plummer, L. N., and Busenberg, E., 1990, Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems: Geochimica et Cosmochimica Acta, v. 54, p. 267–282.

Gresens, R. L., 1981a, The aqueous solubility product of solid solutions: 1) stoichiometric saturation; partial and total solubility product: Chemical Geology, v. 32, p. 59–72.

———— 1981b, The aqueous solubility product of solid solutions: 2) extension to binary solutions with stoichiometric coefficients greater than unity; analogy with vapor pressure of a binary liquid solution: Chemical Geology, v. 32, p. 73–86.

Guggenheim, E. A., 1937, Theoretical basis of Raoult's law: Transactions of the Faraday Society, v. 33, p. 151–159.

———— 1952, Mixtures: London, Oxford University Press, 270 p.

Henderson, L. M., and Kracek, F. C., 1927, The fractional precipitation of barium and radium chromates: Journal of the American Chemical Society, v. 49, p. 739–749.

Högfeldt, E., 1982, Stability Constants of Metal-Ion Complexes. Part A, *in* Inorganic Ligands: IUPAC Chemical Data Series, No. 21: New York, Pergamon Press, 310 p.

King, M. B., 1969, Phase Equilibrium in Mixtures: New York, Pergamon Press, 584 p.

Kirgintsev, A. N., and Trushnikova, L. N., 1966, Thermodynamics of MCl-MBr solid solutions: Russian Journal of Inorganic Chemistry, v. 11, p. 1250–1255.

Kittrick, J. A., 1973, Mica-derived vermiculites as unstable intermediates: Clays and Clay Mineralogy, v. 21, p. 479–488.

Lafon, G. M., 1978, Discussion of "Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase — example: the magnesian calcites": American Journal of Science, v. 274, p. 1455–1468.

Lippmann, F., 1977, The solubility product of complex minerals, mixed crystals and three-layer clay minerals: Neues Jahrbuch für Mineralogie Abhandlung, v. 130, no. 3, p. 243.

———————— 1980, Phase diagrams depicting the aqueous solubility of binary mineral systems: Neues Jahrbuch für Mineralogie Abhandlung, v. 139, no. 1, p. 1–25.

———————— 1982a, Stable and metastable solubility diagrams for the system $CaCO_3$ — $MgCO_3$ — H_2O at ordinary temperature: Bulletin de Mineralogie, v. 105, p. 273–279.

———————— 1982b, Nucleation and polymorphic precipitation of carbonate minerals: Estudios Geologica, v. 38, p. 199–208.

Lukkari, O., and Lukkari, H., 1972, The solubility of barium chromate in sodium perchlorate and potassium chloride solutions: Suomen Kemistilehti, v. 45, part B, p. 6–10.

Mackenzie, F. T., Bischoff, W. D., Bishop, F. C., Loijens, M., Schoonmaker, J., and Wollast, R., 1983, Magnesian calcites: low temperature occurrence, solubility and solid-solution behavior *in* Reeder, R. J., ed., Carbonates: Mineralogy and Chemistry: Reviews in Mineralogy, v. 11, p. 97–144.

Margules, M., 1895, Uber die Zussamensetzung der gesättigten Dämpfe von Mischungen: Kaiserliche Akademie der Wissenschaften, Sitzungsberichte, Mathematich Naturwissenschaftlichen Klasse, Wien, v. 104, Abteil IIa, p. 1243–1278.

McIntyre, W. L., 1963, Trace element partition coefficients-a review of theory and applications to geology: Geochimica et Cosmochimica Acta, v. 27, p. 1209–1264.

Michard, G., 1986, Dissolution d'une solution solide: compléments et corrections: Bulletin de Mineralogie, v. 109, p. 239–251.

Michard, G., and Ouzoukian, G., 1978, Cinétique chimique — dissolution d'une solution solide. étude preliminaire: Comptes Rendus de l'Academie des Sciences de Paris, v. 287, no. 10, Serie C, p. 397.

Moreno, E. C., Kresak, M., and Zahradnik, R. T., 1977, Caries research, v. 11 (Suppl.), p. 142.

Nernst, W., 1891, Distribution of a substance between two solvents and between solvent and vapor: Zeitschrift für Physikalische Chemie, v. 8, p. 110–139.

Palache, C., Berman, H., and Frondel, C., 1951, Dana's System of Mineralogy. II: New York, John Wiley & Sons, 834 p.

Pitzer, K. S., 1979, Theory: ion interaction approach, *in* Pytkowicz, R. M., ed., Activity Coefficients in Electrolyte Solutions, v. 1: Boca Raton, Florida, CRC Press, p. 157–208.

Plummer, L. N., and Busenberg, E., 1982, The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O: Geochimica et Cosmochimica Acta, v. 46, p. 1011–1040.

———————— 1987, Thermodynamics of aragonite — strontianite solid solutions: results from stoichiometric dissolution at 25 and 76 C: Geochimica et Cosmochimica Acta, v. 51, p. 1393–1411.

Plummer, L. N., and Mackenzie, F. T., 1974, Predicting mineral solubility from rate data: Application to the dissolution of magnesian calcites: American Journal of Science, v. 274, p. 61–83.

Plummer, L. N., Parkhurst, D. L., Fleming, G. W., and Dunkle, S. A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines: U.S. Geological Survey, Water Resources Investigations Report 88-4153, 310 p.

Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics: London, Longmans, Green & Co Ltd, 543 p.

Redlich, O., and Kister, A. T., 1948, Algebraic representation of thermodynamic properties and the classification of solutions: Industrial and Engineering Chemistry, v. 40, no. 2, p. 345–348.

Saxena, S. K., 1973, Thermodynamics of Rock-Forming Solutions: Berlin, Springer-Verlag, 188 p.

Schuberth, H., 1977, Alyotropy — the analog to azeotropy: International Chemical Engineering, v. 17, p. 75–79.

Simons, E. L., Orlick, C. A., and Vaughan, P. A., 1952, A study of the solubility limits at 35° in the system NaBr-NaCl: Journal of the American Chemical Society, v. 74, p. 5264–5266.

Stoessell, R. K., and Carpenter, A. B., 1986, Stoichiometric saturation tests of the $NaCl_{1-x}Br_x$ and $KCl_{1-x}Br_x$: Geochimica et Cosmochimica Acta, v. 50, p. 1465–1474.

Swalin, R. A., 1972, Thermodynamics of Solids: New York, John Wiley & Sons, 387 p.

Thompson, J. B. Jr., and Waldbaum, D., 1969, Analysis of the two-phase region halite-sylvite in the system NaCl-KCl: Geochimica et Cosmochimica Acta, v. 33, p. 671–690.

Thorstenson, D. C., and Plummer, L. N., 1977, Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous-phase; example: the magnesian calcites: American Journal of Science, v. 277, p. 1203–1223.

Urusov, V. S., 1974, Energetic criteria for solid solution miscibility gap calculations: Bulletin de la Societé Française de Mineralogie et de Cristallographie, v. 97, p. 217–222.

Walter, L., and Morse, J., 1984, Magnesian calcite stabilities: a reevaluation: Geochimica et Cosmochimica Acta, v. 48, p. 1059–1069.

Wilson, G. M., 1964, Vapor-Liquid Equilibrium. XI. A new expression for the excess free energy of mixing: Journal of the American Chemical Society, v. 86, p. 127–130.

Wollast, R., and Reinhard-Derie, D., 1977, Equilibrium and mechanism of dissolution of Mg-calcites *in* Andersen, N. R. and Malahoff, A., eds., The Fate of Fossile Fuel CO_2 in the Oceans: New York, Plenum Press, p. 479–493.