COMMENT

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

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INTRODUCTION

Glynn and Reardon (1990) presented a thermodynamic derivation of equilibrium, stoichiometric saturation, and primary saturation states in binary solid-solution aqueous-solution systems.

We agree with the results of this paper but would like to clarify and extend some of the concepts involved. The present comment discusses the following topics:

1. The thermodynamic properties of equilibrium and stoichiometric saturation states can be derived in a unifying way, since they correspond to global or constrained minima of the total Gibbs function of the system.
2. Stoichiometric saturation is a constrained metastable equilibrium state characterized by equal molar Gibbs functions of solid and solute species.
3. Tests for thermodynamic consistency and the attainment of the various equilibria are reviewed.
4. Graphical representations of solid-solute phase equilibria in Lippmann and $\phi\Sigma m$ diagrams are discussed.

THERMODYNAMIC BASIS OF SOLID-SOLUTE PHASE EQUILIBRIA

The thermodynamic properties of equilibrium and stoichiometric saturation states can be derived from a unifying point of view (Königsberger and Gamsjäger, 1987). Consider the dissolution reaction of n moles $B_{(1-x_0)}C_{x_0}A$ with m moles H_2O

$$\begin{aligned} n\mathrm{B}_{(1-x_0)}\mathrm{C}_{x_0}\mathrm{A}_{(s)} \xrightarrow{m\mathrm{H_2O}} & (n-\xi)\mathrm{B}_{(1-x)}\mathrm{C}_x\mathrm{A}_{(s)} \\ & + \{n(1-x_0)-(n-\xi)(1-x)\}\mathrm{B}^+_{(aq)} \\ & + \{nx_0-(n-\xi)x\}\mathrm{C}^+_{(aq)} + \xi\mathrm{A}^-_{(aq)}. \end{aligned} \tag{1}$$

In eq (1) ξ, x, and x_0 denote the extent of reaction, the mole fraction, and the initial mole fraction of CA in the solid phase. Solid-solute phase equilibria can be calculated if the total Gibbs function G of the system is known. If ξ and x are chosen as independent variables, G will read

$$\begin{aligned} G = {} & (n-\xi)[(1-x)\mu^s_{BA} + x\mu^s_{CA}] \\ & + [n(1-x_0)-(1-x)(n-\xi)]\mu^{aq}_{B^+} + [nx_0 - x(n-\xi)]\mu^{aq}_{C^+} + \xi\mu^{aq}_{A^-} \\ & + m\mu_{H_2O}. \end{aligned} \tag{2}$$

It is a general equilibrium condition that G remains unchanged during any infinitesimal process occurring at constant temperature and pressure, that is,

$$dG = (\partial G/\partial \xi)_x d\xi + (\partial G/\partial x)_\xi dx = 0. \tag{3}$$

Condition (3) can be satisfied in four different ways, and two of them are important for the present discussion, namely,

$$(\partial G/\partial \xi)_x = 0 \quad \text{(IA)} \quad \text{and} \quad (\partial G/\partial x)_\xi = 0, \tag{IB}$$

$$(\partial G/\partial \xi)_x = 0 \quad \text{(IIA)} \quad \text{and} \quad dx = 0. \tag{IIB}$$

From this unified approach the properties of the system can be derived in a thermodynamically rigorous way for:

(I) thermodynamic equilibrium, where both ξ and x are free to vary, and

(II) stoichiometric saturation, where x will remain constant because diffusion in the solid phase, precipitation of a secondary solid solution, and recrystallization from the aqueous solution are kinetically inhibited.

If the Gibbs-Duhem equation is taken into account a standard procedure (for example, Acree, 1986) will yield

$$(\partial G/\partial \xi)_x = [(1-x)\mu^{aq}_{B^+} + x\mu^{aq}_{C^+} + \mu^{aq}_{A^-}] - [(1-x)\mu^{s}_{BA} + x\mu^{s}_{CA}] \tag{4}$$

and

$$(\partial G/\partial x)_\xi = (1-\xi)(\mu^{s}_{CA} - \mu^{s}_{BA} - \mu^{aq}_{C^+} + \mu^{aq}_{B^+}). \tag{5}$$

Combining eqs (4) and (5) with conditions (IA) and (IB) leads to the well-known simultaneous equality of chemical potentials of corresponding solid and solute species

$$\mu^{s}_{BA} = \mu^{aq}_{B^+} + \mu^{aq}_{A^-} \quad \text{and} \quad \mu^{s}_{CA} = \mu^{aq}_{C^+} + \mu^{aq}_{A^-}. \tag{6}$$

Conditions (IIA) and (IIB) result in

$$(1-x)\mu^{aq}_{B^+} + x\mu^{aq}_{C^+} + \mu^{aq}_{A^-} = (1-x)\mu^{s}_{BA} + x\mu^{s}_{CA} \quad \text{and} \quad dx = 0. \tag{7}$$

With the usual definitions of solubility products and activities (aqueous activities are indicated by braces), condition (IA) as well as (IIA) results in

$$(\{B^+\}\{A^-\})^{(1-x)}(\{C^+\}\{A^-\})^x = (K_{BA}a_{BA})^{(1-x)}(K_{CA}a_{CA})^x \overset{\text{def}}{=} K_{eq}(x). \tag{8}$$

Condition (IB) leads to an expression for the distribution coefficient D

$$D = \frac{x/(1-x)}{[C^+]/[B^+]} = \frac{K_{BA}f_{BA}\gamma_{C^+}}{K_{CA}f_{CA}\gamma_{B^+}}, \tag{9}$$

where f_j and γ_j denote activity coefficients of component j in the solid and aqueous phase, respectively. Eq (6) as well as eqs (8) and (9) results in the

basic conditions defining thermodynamic equilibrium in the system BA–CA–H_2O:

$$\begin{aligned}\{B^+\}\{A^-\} &= K_{BA}a_{BA}\\ \{C^+\}\{A^-\} &= K_{CA}a_{CA}.\end{aligned} \tag{10}$$

Whereas conditions (IA) and (IIA) which lead to eq (8) are equal for equilibrium and stoichiometric saturation, in the latter case condition (IIB), that is constant composition of the solid phase during the dissolution process, is essential. Statements like "an aqueous-solution at equilibrium with respect to a solid $B_{(1-x)}C_xA$ will also be at stoichiometric saturation with respect to same solid" (Glynn and others, 1990) may be misleading. They refer to eq (8); but condition (IIB) is in general not satisfied for equilibrium states. Note in addition that for equilibrium states constant $K_{eq}(x)$ values cannot be observed when the initial conditions are varied. In this case, "$K_{eq}(x)$" serves, however, as a shorthand notation of the left side of eq (8).

From eq (8) the molar Gibbs energy of mixing of the solid phase follows immediately

$$\begin{aligned}\Delta_{mix}G/RT &= (1-x)\ln a_{BA} + x\ln a_{CA}\\ &= \ln K_{eq}(x) - (1-x)\ln K_{BA} - x\ln K_{CA}.\end{aligned} \tag{11}$$

Provided thermodynamic equilibrium or stoichiometric saturation can be experimentally demonstrated, $\Delta_{mix}G$ and derived thermodynamic properties (activities) of the solid solution are unequivocally determined.

It should be mentioned that an expression equivalent to eq (11) was already employed by McCoy and Wallace (1956) for the calculation of $\Delta_{mix}G$ of KCl–KBr solid solutions from solubility and isopiestic data.

Note that in our derivation as opposed to Glynn and Reardon (1990) it is not necessary to define standard chemical potentials and activities of solid solutions reacting with fixed composition.

If experimental $K_{eq}(x)$ values are available, the integral quantity $\Delta_{mix}G$ can be determined directly (Gamsjäger, 1985; Glynn and Reardon, 1990). The estimation of $\partial \ln K_{eq}(x)/\partial x$ for the calculation of partial quantities a_i as proposed by Thorstenson and Plummer (1977) may unnecessarily introduce numerical errors. Because activity coefficients f_i obtained in this way are derived from the same $\Delta_{mix}G$ function, they must pass a necessary, though not sufficient, criterion for thermodynamic consistency.

CONSISTENCY TESTS

Test I.—Consider the Gibbs-Duhem equation of a binary phase in the following form

$$(1-x)\mathrm{d}\ln f_{BA} + x\mathrm{d}\ln f_{CA} = 0. \tag{12}$$

Rearrangement and integration of eq (12) results in

$$\int_0^1 \ln (f_{CA}/f_{BA})\, dx = 0. \tag{13}$$

Eq (13) is the basis of the so-called "equal-area" test for separately determined activity coefficients (McGlashan, 1979). It should be noted that the integral (13) may be close to zero even when the data are grossly inconsistent thermodynamically; for example, if $\ln f_{BA} = ax$ and $\ln f_{CA} = a(1 - x)$ the integral is zero in spite of those functions failing to satisfy the Gibbs-Duhem eq (12).

From the definition of the excess Gibbs energy of mixing $G^{E(s)}$ of the solid phase

$$G^{E(s)}/RT = (1 - x) \ln f_{BA} + x \ln f_{CA} \tag{14}$$

one obtains

$$\frac{\partial G^{E(s)}/RT}{\partial x} = \ln (f_{CA}/f_{BA}) \tag{15}$$

and hence

$$\int_0^1 \frac{\partial G^{E(s)}}{\partial x} dx = G^{E(s)}(x = 1) - G^{E(s)}(x = 0) = 0, \tag{16}$$

which is an alternative derivation of the equal-area test.

In their discussion of Thorstenson and Plummer's (1977) equations for the calculation of solid-phase activities, Glynn and Reardon (1990) noted in their eq (30) that

$$\frac{\partial G^{E(s)}}{\partial x} = RT\left[\frac{\partial \ln K_{eq}(x)}{\partial x} + \ln\left(\frac{K_{BA}}{K_{CA}}\right) + \ln\left(\frac{1 - x}{x}\right)\right]. \tag{17}$$

Then, eq (18) follows

$$\int_0^1 \left[\frac{\partial \ln K_{eq}(x)}{\partial x} + \ln\left(\frac{K_{BA}}{K_{CA}}\right) + \ln\left(\frac{1 - x}{x}\right)\right] dx = 0. \tag{18}$$

In their experimental study of aragonite-strontianite solubilities, Plummer and Busenberg (1987) presented estimated values of $\partial \log K_{eq}(x)/\partial x$ at 25° and 76°C. Numerical evaluation of the integral (18) can be performed, for example, with the NAG subroutine D01GAF (NAG: see references) and yields with the 25°C data of Plummer and Busenberg (1987) a value of $\int_0^1 \ln (f_{CA}/f_{BA})dx = 0.025$. In figure 1 these data are shown along with the corresponding smoothed function that must satisfy the equal-area test in any case, because it has been derived from the subregular mixing model

$$G^{E(s)}/RT = x(1 - x)[a_0 + a_1(2x - 1)] \tag{19}$$

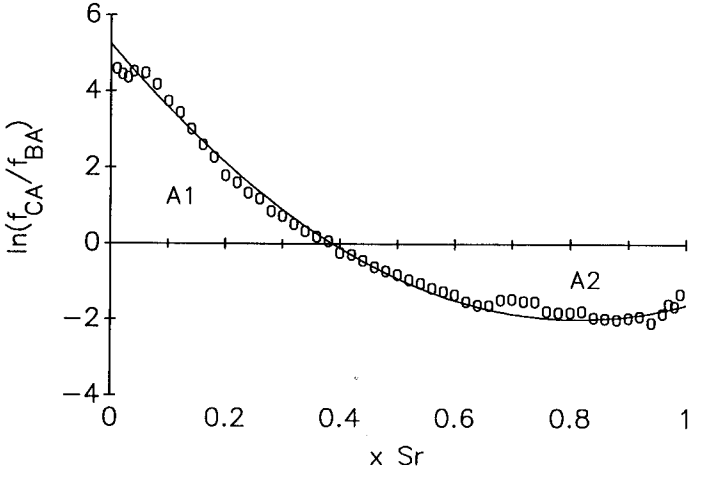

Fig. 1. "Equal-area" test of solid-phase activity coefficient ratios for aragonite–strontianite solid solutions. Solid line was calculated with $G^{E(s)}$ parameters $a_0 = 3.43$ and $a_1 = -1.82$ of eq (19) and satisfies the condition A1 = A2 exactly. Excess parameters and $\partial \log K_{eq}(x)/\partial x$ data valid for 25°C were taken from Plummer and Busenberg (1987).

with Plummer and Busenberg's (1987) parameters $a_0 = 3.42$ and $a_1 = -1.82$.

This test could have been used by Plummer and Busenberg (1987) to check the reliability of their $\partial \log K_{eq}(x)/\partial x$ estimation. However, experimental errors in $\log K_{eq}(x)$ values cannot be detected by this test because a thermodynamically consistent $G^{E(s)}$ function (that is, $G^{E(s)}$ must vanish at $x = 0$ and $x = 1$) can always be fitted to these data. As mentioned above, the direct determination of the integral quantity $G^{E(s)}$ from $\log K_{eq}(x)$ data seems to be preferable.

Test II.—In their Reply to this Comment, Glynn and Reardon (1992) present an elegant evaluation of $G^{E(s)}$ from experimentally determined distribution coefficients D. In order to derive a consistency test, we obtain with expression (9)

$$\int_0^1 \ln D\,dx + \int_0^1 \ln (f_{CA}/f_{BA})\,dx = \ln \left[\frac{K_{BA}\gamma_{C^+}}{K_{CA}\gamma_{B^+}}\right], \qquad (20)$$

provided that the ratio of aqueous activity coefficients can be considered constant. If $\int_0^1 \ln (f_{CA}/f_{BA})dx$ satisfies the equal-area test (13), $\int_0^1 \ln D\,dx$ will be equal to the right-hand side of eq (20). An analogous test for volatility ratios was proposed by Herrington (1947).

Alternatively, Glynn and Reardon (1992) substituted a thermodynamically consistent function for $\ln (f_{CA}/f_{BA})$, that is, $\partial(G^{E(s)}/RT)/\partial x$ with $G^{E(s)}/RT$ from eq (19) and determined the parameters a_0 and a_1 by linear regression. The computed intercept corresponded excellently to the

right-hand side of eq (20), thus confirming the conjecture that the distribution coefficients of Durham, Rock, and Frayn (1953) were thermodynamically consistent.

Test III.—Plummer (1986) suggested the following consistency test, which can be deduced from conditions (IA) and (IB), to check the establishment of equilibrium in the system KCl–KBr–H_2O at 25°C: First, eq (11) can be employed to calculate $G^{E(s)}$ which is converted to activity coefficients f_j. Then eq (9) is used to compute distribution coefficients D which are compared with experimental values. Obviously Plummer (1986) miscalculated aqueous molalities and arrived at the conclusion that equilibrium was not established. Since equilibrium was approached experimentally from two directions, providing strong evidence that it was indeed attained (Durham, Rock, and Frayn, 1953), we have recalculated D values according to the method proposed in the next section and present them in table 1A and B. Good agreement between experimental and calculated results was obtained as also shown in figure (6) of Glynn and Reardon (1990).

Thus, Plummer's (1986) test is based on the fact that conditions (IA) and (IB) must be simultaneously satisfied at equilibrium. It can also be visualized in Lippmann diagrams: both tie-lines and corresponding ΣK values must be derivable from one, thermodynamically consistent $G^{E(s)}$ function.

TABLE 1

A. *The system KCl–KBr–H_2O at 25°C; calculated values*

No.[1]	x_s	x_{aq}	log ΣK	m_{tot}/mol kg^{-1}	D
2	0.050	0.234	1.006	5.278	0.172
3	0.179	0.456	1.120	5.832	0.260
4	0.261	0.514	1.149	5.980	0.334
5	0.479	0.592	1.179	6.129	0.634
6	0.732	0.686	1.185	6.139	1.250
7	0.894	0.819	1.167	5.998	1.860

[1]No. refers to table 1 of Durham, Rock, and Frayn (1953).

B. *The system KCl–KBr–H_2O at 25°C; experimental values*

No.[2]	x_s	x_{aq}	log ΣK	m_{tot}/mol kg^{-1}	D
1	0.000	0.000	0.904	4.816	...
2	0.048	0.234	1.006	5.275	0.165
3	0.188	0.452	1.118	5.822	0.281
4	0.274	0.508	1.146	5.965	0.366
5	0.484	0.589	1.178	6.127	0.655
6	0.729	0.687	1.185	6.136	1.230
7	0.891	0.821	1.167	5.997	1.780
8	1.000	1.000	1.129	5.737	...

[2]Average values of A and B runs of Durham, Rock, and Frayn (1953, table 1) are given.

Test IV.—Stoichiometric saturation can be demonstrated only experimentally, for example, by arriving at the same K_{eq} after variation of initial conditions. For carbonate systems, the pH variation method (Schindler, 1963) has been employed to determine $^*K_{ps0}(x)$'s of $Co_{(1-x)}\ Mn_xCO_3$ solid solutions (Gamsjäger, 1985) and the metastable compound huntite $Ca_{0.25}Mg_{0.75}CO_3$ (Könisberger and Gamsjäger, 1987). Equilibration with "spiked" solutions, as suggested by Garrels and Wollast (1978), resulted in constant $K_{eq}(x)$ values for magnesian calcites of composition x (Walter and Morse, 1984) and in a constant $^*K_{ps0}$ for huntite (Königsberger and Gamsjäger, 1987).

Again, it is the only consistency criterion that $G^{E(s)}$ must vanish at $x = 0$ and $x = 1$.

CALCULATION OF EQUILIBRIUM STATES

Thermodynamic equilibrium.—The values of ξ and x at equilibrium can be calculated by minimizing the total Gibbs function given by

$$G = G_s + G_{aq} + G_{H_2O}, \tag{21}$$

where

$$G_s/RT = (n - \xi)[(1 - x)\ln(1 - x) + x \ln x + G^{E(s)}/RT], \tag{22}$$

$$\begin{aligned} G_{aq}/RT = {} & [n(1 - x_0) - (1 - x)(n - \xi)] \\ & \ln\left\{\frac{1000}{mM_{H_2O}}[n(1 - x_0) - (1 - x)(n - \xi)]\gamma_{B^+}\right\} \\ & + [nx_0 - (n - \xi)x] \ln\left\{\frac{1000}{mM_{H_2O}}[nx_0 - (n - \xi)x]\gamma_{C^+}\right\} \\ & + \xi \ln\left\{\frac{1000}{mM_{H_2O}}\xi\gamma_{A^-}\right\} \\ & - [n(1 - x_0) - (n - \xi)(1 - x)] \ln K_{BA} \\ & - [nx_0 - (n - \xi)x] \ln K_{CA}, \end{aligned} \tag{23}$$

$$G_{H_2O}/RT = -2\xi\phi. \tag{24}$$

It should be emphasized that constant terms ($m\mu^{\ominus}_{H_2O}$) and common constant factors (RT) are irrelevant for G minimization.

The osmotic coefficient ϕ and the activity coefficients γ_j may be calculated from the Pitzer equation (Harvie, Møller, and Weare, 1984). In eqs (22–24) $M_{H_2O} = 18.015$ g mol^{-1}; n, m, ξ, x, and x_0 are defined by reaction (1). The minimum of G can be easily computed with a simple FORTRAN program employing, for example, the NAG subroutine E04JAF (NAG: see references). Equilibrium states of KCl–KBr–H_2O at 25°C with total compositions given by Durham, Rock, and Frayn (1953) were calculated with Pitzer coefficients β_0, β_1, and C^{ϕ} from Pitzer and

Mayorga (1973), and the $G^{E(s)}$ function (19) of the solid phase, where the parameters $a_0 = 1.396 \pm 0.005$ and $a_1 = -0.083 \pm 0.012$ were obtained via eq (11). Calculated and experimental values are given in table 1A and B, respectively.

Stoichiometric saturation.—The value of ξ at stoichiometic saturation can be calculated by minimizing the total Gibbs function (21) under the constraint $x = x_0$, that is,

$$G_s/RT = (n - \xi)[(1 - x_0) \ln (1 - x_0) + x_0 \ln x_0 + G^{E(s)}/RT], \quad (25)$$

$$G_{aq}/RT = [(1 - x_0)\xi] \ln \left\{ \frac{1000}{mM_{H_2O}} [(1 - x_0)\xi]\gamma_{B^+} \right\} + (x_0\xi) \ln \left\{ \frac{1000}{mM_{H_2O}} (x_0\xi)\gamma_{C^+} \right\} + \xi \ln \left\{ \frac{1000}{mM_{H_2O}} \xi\gamma_{A^-} \right\} - [(1 - x_0)\xi] \ln K_{BA} - (x_0\xi) \ln K_{CA}, \quad (26)$$

$$G_{H_2O}/RT = -2\xi\phi. \quad (27)$$

Again, the minimum of this function with respect to ξ can be calculated by a simple computer program.

GRAPHICAL REPRESENTATION

Lippmann diagrams.—To describe the aqueous solubility of binary mineral systems Lippmann (1980) introduced a new kind of solid-solute phase diagrams and defined the total solubility product

$$\Sigma K = (\{B^+\} + \{C^+\})\{A^-\} = (1 - x) f_{BA} K_{BA} + x f_{CA} K_{CA} \quad (28)$$

and activity fractions

$$x_{act} = \{C^+\}/(\{B^+\} + \{C^+\}) = \{C^+\}\{A^-\}/\Sigma K = x f_{CA} K_{CA}/\Sigma K. \quad (29)$$

Homogeneous equilibria in the aqueous phase are not taken into account by reaction (1); hence, activity fractions will be equal to relative mole fractions

$$x_{aq} = [C^+]/([B^+] + [C^+]) \quad (30)$$

if and only if $\gamma_{B^+} = \gamma_{C^+}$ ([ ] denotes molality). It is neither essential nor always convenient to use solubility products in Lippmann diagrams; any other solubility variable such as ${}^*K_{ps0} = \{M^{2+}\}p_{CO_2}\{H^+\}^{-2}$ serves the same purpose, and the respective equations can be modified accordingly. Although ΣK was intended to depict the states of thermodynamic equilibrium it is useful for a representation of stoichiometric saturation as well

(Gamsjäger, 1985; Königsberger and Gamsjäger, 1987, 1990a,b; Glynn and Reardon, 1990; Glynn and others, 1990).

The equal-G curve.—In the experimental investigation of $Co_{(1-x)}Mn_xCO_3$ solid solutions (Gamsjäger, 1985), it was shown that stoichiometric saturation corresponds to equal molar G functions of solid and solutes.

This result follows indeed from eq (7) when $x = x_{aq}$ (Königsberger and Gamsjäger, 1990b). Stoichiometric saturation was identified as a metastable equilibrium state and recognized as a further example of Oonk's (1981) equal-G approach to diffusionless phase transitions (Königsberger and Gamsjäger, 1987). Under the constraint of constant composition of the solid phase the two-phase area referring to thermodynamic equilibrium of, for example, $\ln \Sigma K - x$ phase diagrams shrinks to a one dimensional two-phase equal-G curve (EGC). In a general discussion of phase diagrams Hillert (1985) recently stressed the phenomenon of constrained equilibria.

Eqs (8) and (29) result in eq (31)

$$\Sigma K_{ss} = \frac{K_{eq}(x)}{(1 - x_{act})^{(1-x)} x_{act}^{x}}, \tag{31}$$

which defines soluti of congruently soluble solid solutions or compounds at stoichiometric saturation. Eq (31) which corresponds to Glynn and Reardon's (1990) eq (56) was already employed by Königsberger and Gamsjäger (1987) for the graphical representation of "spiked" solutions stoichiometrically saturated with huntite. Lippmann (1980) previously derived eq (31) for stoichiometric compounds, that is, cases in which $(1 - x)/x$ or its reciprocal are small integer numbers or can be converted to integers by multiplication with small integer numbers.

Eq (11) and the condition $x = x_{act}$ result in eq (32) which relates ΣK unambiguously to the excess Gibbs energy of mixing of the solid phase $G^{E(s)}$, if $x = x_{act} = x_{aq}$, since in this case it equals the EGC,

$$\ln \Sigma K_{EGC}(x) = (1 - x) \ln K_{BA} + x \ln K_{CA} + G^{E(s)}/RT. \tag{32}$$

Even when $x_{act} \neq x_{aq}$ equal-G states can be represented by Lippmann diagrams to a very good approximation if $\Sigma K_{EGC}(x)$ is plotted versus the mole fraction x of the *solid phase*. For the system KCl–KBr–H_2O hypothetical $\Sigma K_{EGC}(x)$ values have been calculated from G minimization constrained to the condition $x = x_{aq}$ as well as from eq (32) where the condition $x = x_{act}$ is valid. Although x_{aq} and x_{act} differ by 0.02 units in x, the difference in $\Sigma K_{EGC}(x)$ is negligible because of the shallow minimum of function (31).

G minimization provides a direct proof that stoichiometric saturation is a metastable equilibrium state, since for the same initial conditions

equilibrium states correspond to a lower G value than stoichiometric saturation states (fig. 2).

Eq (32) is equivalent to Glynn and Reardon's (1990) "minimum stoichiometric saturation curve" and was already used by Gamsjäger (1985) to calculate $G^{E(s)}$ of $Co_{(1-x)}Mn_xCO_3$ solid solutions which are actually stoichiometrically saturated in aqueous acidic media at 323K for at least one week. Eq (32) is also fundamental for the application of a chemical potentiometer described elsewhere (Königsberger, Bugajski, and Gamsjäger, 1989; Königsberger and Gamsjäger, 1990a).

As can be seen from eq (32), in $\ln \Sigma K$ (or $\log \Sigma K$) $- x$ (but not in $\Sigma K - x$) diagrams the deviation of $\ln \Sigma K_{EGC}(x)$ (or $\log \Sigma K_{EGC}(x)$) from the straight line connecting the solubility constants of the endmembers is proportional to $G^{E(s)}$.

If in the general case ($x_{aq} \neq x_{act}$) the activity fraction is introduced as the independent variable as in eq (33)

$$G'_{aq}/RT = \ln \Sigma K - (1 - x_{act}) \ln K_{BA} - x_{act} \ln K_{CA} + (1 - x_{act}) \ln (1 - x_{act}) + x_{act} \ln x_{act}, \quad (33)$$

it can be seen that G'_{aq} agrees formally with the molar G function of an ideal, binary phase. Since the solid phase in the present case is also a binary mixture, the method of common tangents to molar G_s and G'_{aq} functions leads to equilibrium values of x and x_{act} (Königsberger and Gamsjäger, 1990b), although Lippmann diagrams actually refer to ternary systems. Therefore, Lippmann diagrams can in general be envisaged as quasi-binary phase diagrams.

Due to this "quasi-idealization" of the aqueous phase, eq (32) as well as the respective solidus and solutus curves depend on the excess Gibbs energy $G^{E(s)}$ of *only* the solid phase and can be represented by explicit functions (Lippmann, 1980; Königsberger and Gamsjäger, 1987; Glynn and Reardon, 1990). However, experimentally determined mole fractions x_{aq} cannot be depicted directly in Lippmann diagrams, they must be converted to activity fractions x_{act} with the corresponding activity coefficients γ_i.

Analysis of Lippmann diagrams.—The following example indicates that unreliable results for $G^{E(s)}$ may be obtained from eq (11).

Makarov and Evstrop'ev (1960) investigated the system KBr–KI–H_2O at 25°C and provided $x - m_{KBr} - m_{KI}$ as well as $\gamma_{\pm KBr}$ and $\gamma_{\pm KI}$ data, where the latter were obtained by the isopiestic method. From these data we have calculated $x - x_{act} - \Sigma K$ values and present them in a Lippmann diagram. The observed miscibility gap $0.16 \leq x \leq 0.89$ (Makarov and Evstrop'ev, 1960) results in the parameters $a_0 = 2.54$ and $a_1 = 0.165$ of the excess G function (19).

Evaluation of $G^{E(s)}$ from eq (11) yields $a_0 = 2.20 \pm 0.06$, $a_1 = 0.08 \pm 0.07$, and miscibility limits of 0.268 and 0.774 which due to the large uncertainty of x do not agree with the experimental results cited above.

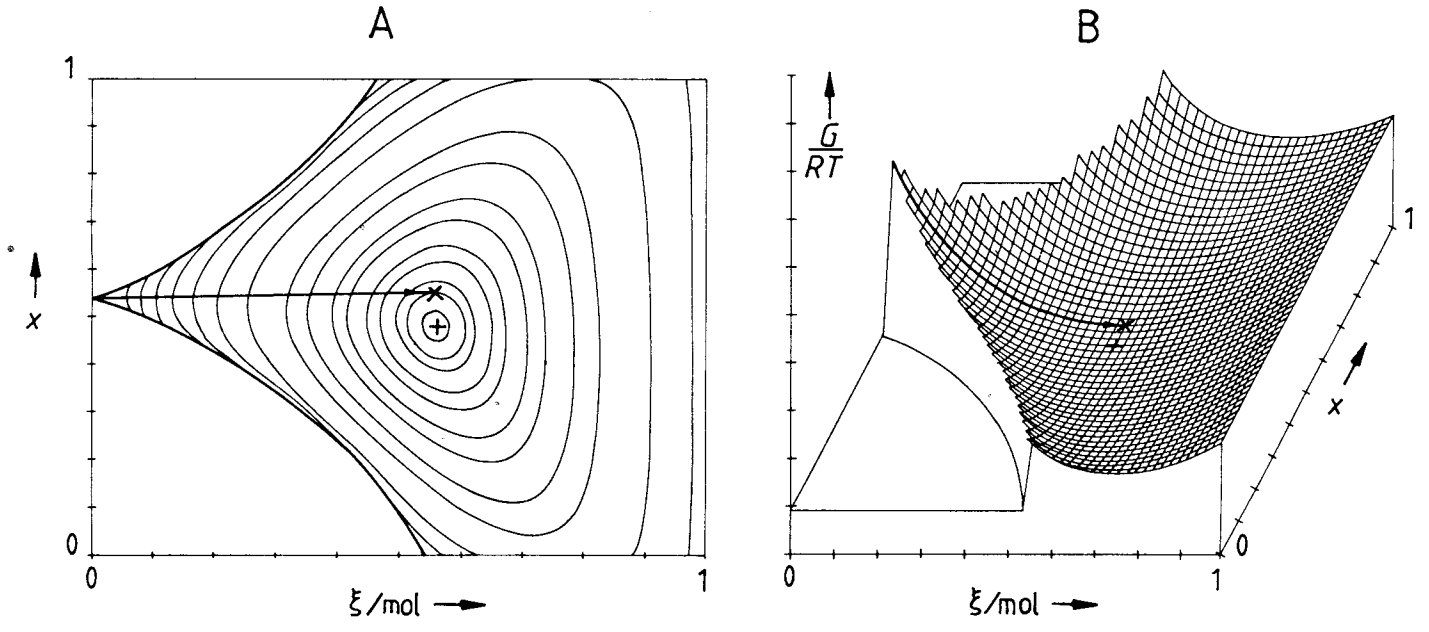

Fig. 2. Contour (A) and axonometric (B) plots of $G(\xi, x)$ for KCl–KBr–H_2 at 25°C. The experimentally observed equilibrium for the initial conditions $x_0 = 0.542$, $n = 1$ mol, and $m = 5.055$ mol (Durham, Rock, and Frayn, 1953, table I, no. 5) corresponds to the absolute minimum of G (+). The hypothetical stoichiometric saturation path (solid arrow) and end-point (×) for the dissolution of a mixed crystal of composition x_0 correspond to the G minimum with respect to ξ under the constraint $x = x_0$. In the "empty" regions $[Cl^-]$ or $[Br^-]$ is negative, thus G does not exist.

Recently, Königsberger and Gamsjäger (1990c) applied Bayesian parameter estimation to the analysis of phase diagrams. A modification of this method for the analysis of Lippmann diagrams uses log ΣK as independent and x and x_{act} as dependent variables. With the experimental miscibility limits as *a priori* information the excess parameters $a_0 = 2.46 \pm 0.05$, $a_1 = 0.14 \pm 0.07$, and calculated miscibility limits of 0.178 and 0.870 are obtained. Experimental data and the calculated phase diagram are shown in figure 3.

However, it should be mentioned that other experimental studies of this system (reviewed by Sangster and Pelton, 1987) as well as a recent semiempirical model (Königsberger and Schrunner, 1989; Königsberger, 1990) suggest a region of demixing skewed toward the KBr side.

A new solid-solute phase diagram.—According to Schmalzried and Pelton's (1973) topological classification, the common basis of phase diagrams are generalized Gibbs-Duhem equations

$$X_{m,1}dY_1 + X_{m,2}dY_2 + X_{m,3}dY_3 + \ldots + X_{m,l}dY_l = 0, \qquad (34)$$

where at equilibrium the potentials Y_i $(T, -P, \mu_i)$ must have the same value in all parts of the system. Furthermore, all the conjugate molar

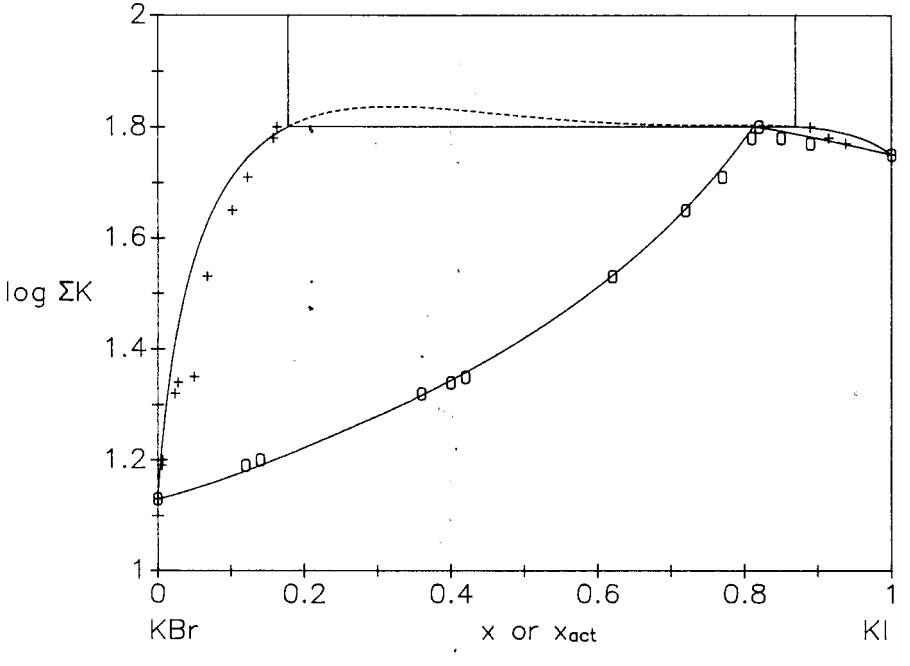

Fig. 3. Lippmann diagram of the system KBr–KI–H_2O at 25°C (solid lines); + solidus, ∘ solutus points (Makarov and Evstrop'ev, 1960). $G^{E(s)}$ parameters of eq (19) are $a_0 = 2.46$ and $a_1 = 0.14$. The solidus inside the miscibility gap (dashed line) is unobservable.

quantities $X_{m,i} = X_i/n$ (S_m, V_m, x_i) have to be defined in the same way, that is, with the same definition of the amount n (Hillert, 1985).

Schmalzried and Pelton (1973) pointed out that three types of equilibrium phase diagrams can be topologically distinguished, provided the potentials $Y_4, Y_5, \ldots, Y_l$ are kept constant:

1. Type I: $Y_j - Y_k$ diagrams,
2. Type II: $Y_j - X_{m,k}$ and $X_{m,j} - Y_k$ diagrams,
3. Type III: $X_{m,j} - X_{m,k}$ diagrams.

Type I is also termed *potential phase diagram*, whereas types II and III are referred to as *molar phase diagrams* (Hillert, 1985). Unary $P-T$ diagrams are of type I, whereas the Gibbs triangle is a type III diagram. Binary $T-x$ and $P-x$ diagrams are of type II, where points of extremum are characterized by equal compositions of both phases (azeotropic or congruent points) and a horizontal common tangent to the one-phase fields (Konovalov rule).

As was emphasized by Hillert (1985), the Konovalov rule does not apply only to composition: Suppose that a linear two-phase field in a Y_j-Y_k diagram shows a Y_k extremum; at this point the two phases must have the same value of $X_{m,j}$ (generalized Konovalov rule).

According to these general considerations, Königsberger and Gamsjäger (1991) derived three types of solid-solute phase diagrams from Gibbs-Duhem equations for binary, ionic solids and the corresponding ternary aqueous solutions. Moreover, they proposed a new, convenient graphical representation of the corresponding solid-solute phase equilibria.

When the osmotic coefficient ϕ of the solvent is introduced, the Gibbs-Duhem equation of the aqueous phase can be written as eq (35)

$$(1 - x_{aq})\mathrm{d} \ln \{B^+\}\{A^-\} + x_{aq}\mathrm{d} \ln \{C^+\}\{A^-\} - \frac{2}{\Sigma m}\mathrm{d}(\phi \Sigma m) = 0. \quad (35)$$

Therefore, $\phi\Sigma m - x - x_{aq}$ diagrams are of type II, extrema are indicative for alyotropic states, and the original Konovalov rule referring to compositions is satisfied. The numerical value of the variable $\phi\Sigma m$ is often close to the solubility Σm of the mixed crystals. Recall that in a ternary system (homo-) alyotropism corresponds to a two-phase equilibrium characterized by equal relative mole fractions, that is, in this case $x = x_{aq}$ (Schuberth, 1977).

On the other hand, a "generalized Gibbs-Duhem equation" of the aqueous phase can formally be derived from definitions (28) and (29)

$$(1 - x_{act})\mathrm{d} \ln \{B^+\}\{A^-\} + x_{act}\mathrm{d} \ln \{C^+\}\{A^-\} - \mathrm{d} \ln \Sigma K = 0. \quad (36)$$

Note, however, that x_{act} is not a molar quantity in the sense of $X_{m,i}$. Together with the Gibbs-Duhem equation of the solid phase and the equilibrium conditions of equal chemical potentials of solid and solute

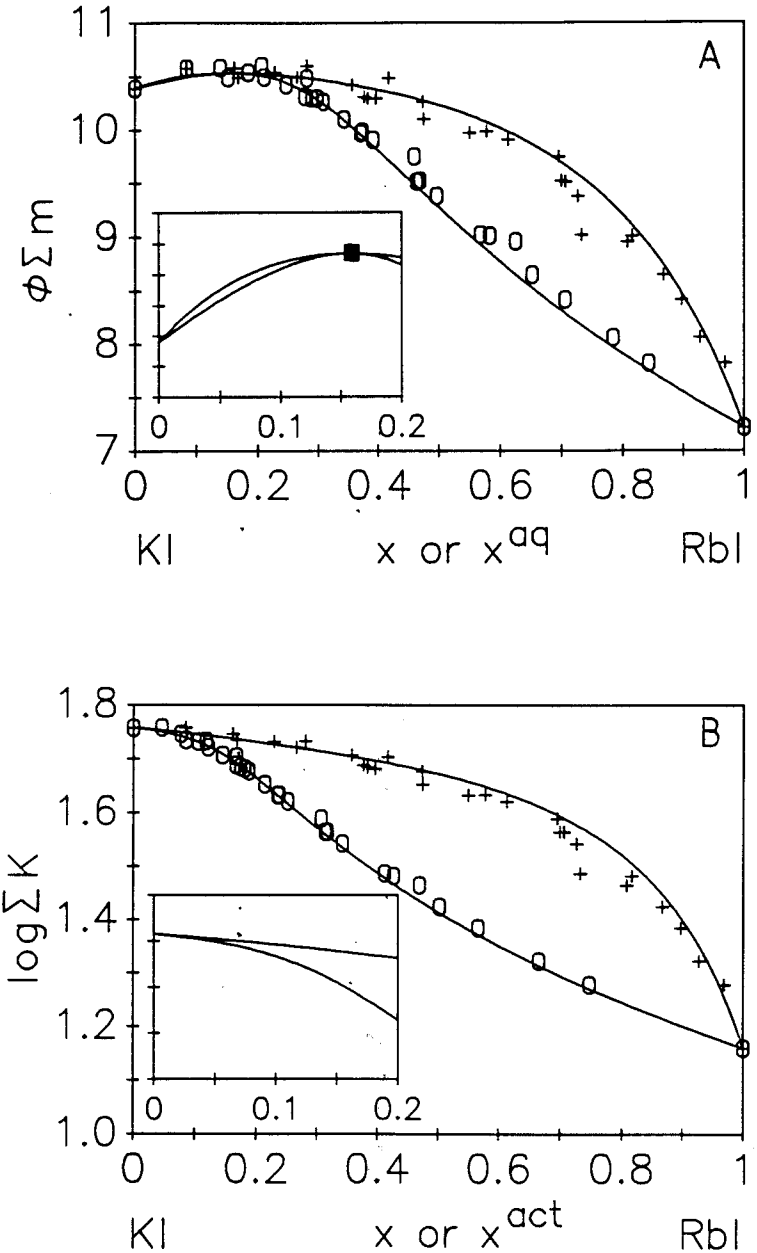

Fig. 4. $\phi\Sigma m$–x–x_{aq} diagram (A) and Lippmann ΣK–x–x_{act} diagram (B) of the system KI–RbI–H_2O at 25°C. + solidus, ∘ solutus points (Makarov and Stupin, 1961). ■ indifferent point. $G^{E(s)}$ parameters of eq (19) are $a_0 = 1.00$ and $a_1 = -0.15$. $G^{E(aq)}$ from Pitzer and Mayorga (1973) where the parameters C^{ϕ}_{KI} and C^{ϕ}_{RbI} have been adjusted to −0.00311 and −0.00189, respectively.

components it follows (Königsberger and Gamsjäger, 1991)

$$x = x_{act} \leftrightarrow \mathrm{d} \ln \Sigma K = 0, \tag{37}$$

that is, in $\ln \Sigma K - x - x_{act}$ diagrams there will be a horizontal tangent to solidus and solutus when the mole fraction in the solid phase and the activity fraction in the aqueous phase are equal. Thus, the "generalized Konovalov rule" applies to this extremum in accordance with eq (36); hence Lippmann diagrams are topologically of type II. However, Lippmann's (1980) original generalization that coinciding solidus and solutus curves in his diagrams indicate alyotropic states is not strictly valid.

In the system KI–RbI–H_2O the Pitzer model predicts $\gamma_{Rb^+}/\gamma_{K^+} \approx 0.5$ (the C^ϕ parameters were slightly adjusted in order to represent measured activities of water up to saturation, compare Makarov and Stupin, 1961). Consequently, $x_{act} - x_{aq} \approx 0.15$ at $x_{aq} \approx 0.5$. As shown in figure 4, the $\phi\Sigma m - x$ diagram exhibits an alyotropic maximum and hence a restriction to the separability of the components by fractional crystallization, whereas in the Lippmann diagram no maximum occurs.

A special situation arises when measurements are carried out in a medium of high, constant ionic strength. In this case the γ_i's and hence ϕ do not depend on m and x_{aq} at all. Then the ionic medium can be chosen as reference system, and the species of interest are forced to behave ideally, that is, concentrations and mole fractions can be employed instead of activities and activity fractions. In these cases, Lippmann diagrams are equivalent to $\phi\Sigma m - x$ diagrams. Eq (32) is valid at $x = x_{aq}$ and represents the equal-G curve.

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REPLY

PIERRE D. GLYNN* and ERIC J. REARDON**

INTRODUCTION

Königsberger and Gamsjäger (1992) present a useful discussion of some of the concepts presented in Glynn and Reardon (1990). Although we agree with most of their comments, the present reply gives some additional remarks and clarifications on the topic of solid-solution aqueous-solution thermodynamics, and on the thermodynamics of the KCl–KBr–H_2O system.

SOLID-SOLUTION AQUEOUS-SOLUTION THERMODYNAMICS: GENERAL REMARKS

The relation between thermodynamic equilibrium and stoichiometric saturation states.—E. Königsberger and H. Gamsjäger present an interesting, and elegant, derivation of the thermodynamic properties of thermodynamic equilibrium and stoichiometric saturation. This derivation was also presented in their excellent paper (Königsberger and Gamsjäger, 1987) on the solubility of huntite ($CaMg_3(CO_3)_4$), a paper that had not previously come to our attention. The derivation first defines the total free-energy function (G) of the system in terms of two independent variables, ξ, the reaction progress variable, and x, the composition of the solid phase, and then sets the equilibrium criterion, $dG(\xi,x) = 0$. Königsberger and Gamsjäger remark that the relation $dG(\xi,x) = 0$ can be satisfied in four possible ways. One solution corresponds to the definition of thermodynamic equilibrium for a system with a variable-composition solid, that is corresponds to the equality of the chemical potentials in the solid and solute species (see eqs 12 and 13 in Glynn and Reardon, 1990). Another solution corresponds to the definition of stoichiometric saturation, that is thermodynamic equilibrium for a system with a fixed-composition solid (represented by eq 14 in Glynn and Reardon and by the requirement, $dx = 0$, inherent in the concept of stoichiometric saturation).

Glynn and others (1990, p. 269) state that "An aqueous-solution at equilibrium[1] with respect to a solid $B_{1-x}C_xA$ will also be at stoichiometric saturation with respect to that same solid." Glynn and Reardon (1990, p. 170) give a similar, slightly more precise statement: "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." As Königsberger and Gamsjäger point out, these statements may be misleading, as the reference to thermodynamic equilibrium implies that the solid is a binary-component solid, whereas the reference to stoichiometric saturation implies that the solid consists of a

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[1] In Glynn and others (1990), the word "equilibrium" is always used in place of "thermodynamic equilibrium," implying a final equilibrium state rather than any possible intermediate metastable equilibrium state.

single component of fixed composition, that is, dx = 0. Glynn and Reardon should have said: "an aqueous solution at thermodynamic equilibrium with respect to a solid $B_{1-x}C_xA$ capable of varying its composition, will also be at stoichiometric saturation with respect to a solid of the same composition $B_{1-x}C_xA$ of fixed and invariant composition" (assuming that the free energies of the two solids, the fixed-composition solid and the invariant-composition solid, are equal).

Königsberger and Gamsjäger state that "constant composition of the solid phase during the dissolution process is essential [to the definition of stoichiometric saturation]" and that "condition (IIB) [that is, dx = 0] is in general not satisfied for equilibrium states." These statements could be thought to imply that thermodynamic equilibrium for a binary solid solution $B_{1-x}C_xA$ can not be attained without varying its composition. This implication would be incorrect, given that an initial aqueous solution composition, with a unique B^+/C^+ ratio for any given concentration of A^- ions, can always be found such that its reaction with a solid $B_{1-x}C_xA$ leads to equilibrium through a congruent dissolution pathway, that is without compositional variation of the solid phase (see Glynn and others, p. 269). Galinier and others (1989) used this principle in trying to measure solid-solution solubilities at thermodynamic equilibrium, thereby calculating solid-solution free energies. Congruent dissolution to thermodynamic equilibrium may even occur in initially pure water, or more generally in a water with a B^+/C^+ ratio closely equal to that in the solid, in the special case of systems where the initial solid has an "alyotropic" composition (for example, a solid with $\chi_{KBr} = 0.676$ in the KCl–KBr–H_2O system, Glynn and Reardon, p. 187).

Königsberger and Gamsjäger remark that Glynn and Reardon's derivation of the relation (eq 24 in Glynn and Reardon, 1990):

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

necessarily includes the definition of the standard chemical potential μ^0_{ss} of the fixed-composition solid $B_{1-x}C_xA$. Although Glynn and Reardon (1990) did introduce the relation between μ^0_{ss} and the endmember chemical potentials μ_{BA} and μ_{CA}, this was done only in order to refer to Thorstenson and Plummer's (1977) original definition of stoichiometric saturation which used μ_{ss} and therefore μ^0_{ss}:

$$\Delta\mu_r = (1 - x)\mu_{B^+} + x\mu_{C^+} + \mu_{A^-} - \mu_{ss} = 0 \quad (2)$$

Eq 14 in Glynn and Reardon (equivalent to eq 7 in Königsberger and Gamsjäger, 1992) could have been used instead, thereby bypassing the need to introduce μ^0_{ss}. Actually, eq 16 in Glynn and Reardon (1990) is equivalent to eq 8 in Königsberger and Gamsjäger. In effect, Königsberger and Gamsjäger's derivation implicitly introduces μ^0_{ss} in the definition of K_{ss} (or $K_{eq}(x)$ in their notation) in eq 8. The term $(K_{BA}\, a_{BA})^{1-x}$ $(K_{CA}\, a_{CA})^x$ is related to μ^0_{ss} as shown in Glynn and Reardon's eq 19. Similarly,

the standard endmember chemical potentials μ^0_{BA} and μ^0_{CA} are implicitly introduced by the solubility products K_{BA} and K_{CA}.

There are now at least three derivations of the relation between thermodynamic equilibrium states and stoichiometric saturation states (Thorstenson and Plummer, 1977, with additions by Plummer and Busenberg, 1987; Königsberger and Gamsjäger, 1987; and Glynn and Reardon, 1990); all three arrive at essentially the same relations, establishing the concept of stoichiometric saturation as a constrained equilibrium state. Königsberger and Gamsjäger's derivation has the merit of formulating thermodynamic equilibrium and stoichiometric saturation states in a unifying way, in terms of the total free energy of the system.

Lippmann diagrams and the importance of the aqueous-solution thermodynamic model.—Phase diagrams (for binary gas/binary liquid systems or for solid/melt systems) are typically constructed in terms of mole fractions (and partial pressures in the case of gas/liquid equilibria). Lippmann diagrams differ from traditional phase diagram representations in that they use aqueous activity products and activity fractions (rather than elemental concentrations and mole fractions) to characterize the aqueous phase. As a result, an aqueous thermodynamic model will be required in the construction of Lippmann diagrams from experimental aqueous-concentration data. Furthermore, two different scales are used for the abscissa on a Lippmann diagram: (1) an activity-fraction scale relating to the aqueous-phase composition, and (2) a mole-fraction scale defining the solid-phase composition. In contrast, traditional phase diagrams use a single mole fraction scale to define the composition of all phases in the system.

Königsberger and Gamsjäger comment that equating aqueous mole fractions (χ_{aq} in their notation) with aqueous activity fractions (χ_{act} or $\chi_{B,aq}$ in our notation) is usually a very good approximation. However, it should be noted that this approximation depends *not only* on the equality of the activity coefficients of B^+ and C^+ but *also* on the difference in the extent of ion pairing and/or complexing of B^+ and C^+ with other ions in the aqueous solution. The effect of speciation on the approximation $\chi_{act} = \chi_{aq}$ is usually minimal, because ions that form complete or nearly-complete solid-solution series often have very similar properties in aqueous solution and therefore commonly have a similar complexing or ion-pairing affinity. Nevertheless, speciation and the composition of the aqueous solution can significantly influence solid-solution aqueous-solution kinetics. Reaction kinetics and mechanistic effects, such as surface poisoning, will determine the closeness to which stoichiometric saturation and/or thermodynamic equilibrium states can be approached in laboratory experiments and maintained in the case of stoichiometric saturation states.

The main problem with the $\chi_{act} = \chi_{aq}$ approximation arises in systems with alyotropic extrema (Schuberth, 1977). As discussed by Königsberger and Gamsjäger (1991, 1992), Lippmann's claim that coinciding solidus and solutus curves indicate alyotropic states is not strictly valid. By

definition, alyotropic points correspond to an equilibrium state for which $\chi_{aq} = \chi_{BA}$, and not $\chi_{act} = \chi_{BA}$. Therefore, coinciding solidus and solutus extrema on Lippmann diagrams should perhaps be called "quasi-alyotropic" points. The difference between χ_{act} and χ_{aq} in such systems is usually small (a difference of 0.02 was calculated by Königsberger and Gamsjäger at the alyotropic point in the KCl–KBr–H_2O system). Königsberger and Gamsjäger, nevertheless, give the example of the KI–RbI system, which has an alyotropic maximum at $\chi_{BA} \approx 0.16$ but does not display it on a Lippmann diagram. In comparison, the $\phi\Sigma m$–x phase diagrams proposed by Königsberger and Gamsjäger (1991, 1992) have the distinct advantage of correctly representing the position of alyotropic extrema.

Binary solid-solution systems with alyotropic extrema should generally be uncommon, despite their occurrence in many binary alkali-halide systems (Königsberger, 1990). First of all, ionic solid solutions should have positive excess enthalpies of mixing (Lippmann, 1980) which should therefore eliminate the possibility of alyotropic minima for true ionic solids (with regular solution behavior). Secondly, in order for an alyotropic maximum to occur in a regular binary solid-solution system, the dimensionless excess-free-energy parameter a_0 has to be smaller than 2, and the endmember solubility-products have to be close to each other. For a "quasi-aloytropic" point to occur, the absolute difference in the natural logarithms of the endmember solubility products ($\Delta\ln K$) must be smaller than the numerical value of a_0 (Lippmann, 1980, p. 12). If a_0 is greater than 2 for a regular solid solution, a miscibility gap will occur, and the computed maximum will fall inside the miscibility gap (the difference in $\Delta\ln K$ must therefore be smaller than 2). In the case of a subregular solution ($a_0 \neq 0$, $a_1 \neq 0$), however, the asymmetry of the excess-free-energy function may allow an alyotropic point to occur outside a miscibility gap.

The $\phi\Sigma m$–x phase diagrams proposed by Königsberger and Gamsjäger (1991, 1992) may be more practical than Lippmann diagrams for some applications in compositionally-simple systems. Nevertheless, by their dependence on the solvent osmotic coefficient ϕ and on endmember solubilities (as opposed to solubility products), $\phi\Sigma m$–x diagrams are not only aqueous-solution specific but also require adoption of an aqueous model or experimental data in the determination of ϕ and Σm as a function of solution composition. The $\phi\Sigma m$–x diagram drawn for a given solid-solution aqueous-solution system will not apply if another component is introduced in the aqueous phase, even if this component is not present to any significant degree in the contacting solid-solution. In contrast, the fact that Lippmann diagrams are based on aqueous ion activities, rather than on concentrations, means that they can be applied to a wide variety of aqueous solutions (as long as the solid phase can be considered a two-component system). For example, the Lippmann diagram for the $CaCO_{3,orth}$–$SrCO_3$–H_2O system (Plummer and others, 1991) will apply to any $CaCO_{3,orth}$–$SrCO_3$–*aqueous-solution* system as long as the

only solid-solution components present are pure $CaCO_{3,orth}$ and pure $SrCO_3$. The introduction of another component, such as sodium sulfate, into the aqueous solution would not require drawing another Lippmann diagram but could significantly change both the osmotic coefficient of the solvent and the solubility of the solid phase(s), thereby requiring a different $\phi\Sigma m$–x diagram than one drawn for the original system.

Solid solutions with more than two components.—In the case of ternary or multicomponent solid solutions, two-dimensional Lippmann diagrams can still be used to estimate solubility behavior as long as the solids can be considered "pseudo binary;" the solids may have more than two components, but for all practical purposes the mole fractions of all components except two can be considered invariant. Busenberg and Plummer (1989) considered two limiting solid-solution series for the magnesian calcite system: one series representing highly-disordered magnesian-calcites incorporating a more or less fixed amount of Na_2SO_4, a second series representing less defective, Na_2SO_4-free solids. The first solid-solution series exhibited overall higher solubilities but lower excess free energies than the second series. By considering these two series, Busenberg and Plummer (1989) were able to place thermodynamic limits on the behavior of magnesian calcites formed in various natural environments. A similar analysis can be used to estimate the maximum effect of "impurities" on the solubility of natural minerals. As a first approximation, but only for want of better thermodynamic data, the aggregate of all impurities may be considered a single component. Estimating the thermodynamic solubilities will then depend on choosing an appropriate "impurity endmember" solubility product and a reasonable excess-free-energy parameter. Techniques for estimating this excess-free-energy parameter are discussed in Glynn (1990).

The concept of "constrained-equilibria," mentioned by Königsberger and Gamsjäger (1991), is perhaps more general than the concept of stoichiometric saturation at least in its original definition (Thorstenson and Plummer, 1977). We suggest that the term "stoichiometric saturation" be reserved for fixed single-composition solids (with any number of components), while the more general concept of "constrained equilibria" could be used to describe saturation states for multicomponent solid solutions, in which sets of two or more components are constrained to react as single components (but only for a limited period of time so as not to violate the definition of a component). Experimental evidence is still needed to document the existence of multicomponent SSAS systems behaving in such a manner.

THERMODYNAMICS OF THE KCL–KBR–H_2O SYSTEM

Any determination of the thermodynamic properties of a solid-solution series, based on solid-solution aqueous-solution data, will depend on the thermodynamic model adopted to characterize the aqueous-solution phase. For the sake of consistency, the aqueous model used should always be reported. Königsberger and Gamsjäger's calculations of

the excess free energies of K(Cl, Br) solid solutions and our own calculations (Glynn and others, 1990; Glynn and Reardon, 1990) are based on the data set of Durham, Rock, and Frayn (1953) and use the same thermodynamic model for the aqueous phase. The PHROPITZ aqueous model (Plummer and others, 1988), used by Glynn and others (1990) and Glynn and Reardon (1990), is based on the β^0, β^1, and C^ϕ Pitzer coefficients tabulated by Pitzer and Mayorga (1973), which Königsberger and Gamsjäger also claim to have used. The KCl–KBr–H_2O aqueous-solution model in PHRQPITZ was thoroughly tested by Pummer (1986) and predicted within 0.15 percent or better the experimental osmotic coefficients found by Covington and others (1968). It is therefore not surprising that Königsberger and Gamsjäger's calculation of the a_0 and a_1 excess-free-energy parameters ($a_0 = 1.396 \pm 0.005$, $a_1 = -0.083 \pm 0.012$) are very close to our own calculated values ($a_0 = 1.40 \pm 0.02$, $a_1 = -0.08 \pm 0.03$, Glynn and others, 1990).

There is considerable supporting evidence for the excess-free-energy parameter values calculated by Glynn and others (1990) and Königsberger and Gamsjäger (1991; see also Königsberger, 1990, 1991) for KCl–KBr solid solutions. These same parameter values were used in Glynn and Reardon (1990) to confirm the good agreement between the data set of Durham, Rock, and Frayn (1953) and those of Amadori and Pampanini (1911) and Flatt and Burkhardt (1944). Kirgintsev and Trushnikova (1966) calculated a value of $a_0 = 1.3$ ($a_1 \equiv 0$) for the KCl–KBr series, based on the concordant data of Durham, Rock, and Frayn (1953), Flatt and Burkhardt (1944), Amadori and Pampanini (1911), Boeke (1908), and on the isopiestic data of McCoy and Wallace (1956a). Sangster and Pelton (1987) using the free-energy calculations of McCoy and Wallace (1956b), based on the KCl–KBr–H_2O experiments of Durham, Rock, and Frayn (1953) and Flatt and Burkhardt (1944), give the function, $G^E = (3300 \pm 170)\ \chi_{KCl}\chi_{KBr}$ Joules/mole at 25°C, which corresponds to $a_0 = 1.33$. Sangster and Pelton (1987) also report a function for the excess enthalpy of mixing, $H^E = (3780 \pm 400)\ \chi_{KCl}\ \chi_{KBr}$ Joules/mole at 25°C, derived from various calorimetric data (Fontell, 1939; Hovi, 1948; Popoff and Jaworskaja, 1933; Popoff, 1930; Ivankina, 1958; Fontell, Hovi, and Mikkola, 1949). If the excess-entropy of mixing (S^E) can be assumed close to 0, as Sangster and Pelton suggest, the calorimetric data yield a value of $a_0 = 1.52 \pm 0.17$ (assuming a regular solid-solution model: see Guggenheim, 1937, 1952; Prigogine and Defay, 1954).

In the absence of an available thermodynamic model for the aqueous phase, distribution coefficient (D_{Br^-}) versus solid-phase mole-fraction plots can often yield good estimates of the thermodynamic mixing properties of a solid-solution series. Distribution coefficients for the KBr–KCl system can be defined as:

$$D_{Br^-} = \frac{\chi_{KBr}/\chi_{KCl}}{m^T_{Br^-}/m^T_{Cl^-}} = \frac{K_{KCl}\gamma_{Br^-}(\sigma_{Cl} + 1)}{K_{KBr}\gamma_{Cl^-}(\sigma_{Br} + 1)}\frac{\gamma_{KCl}}{\gamma_{KBr}} \qquad (3)$$

where $m^T_{Cl^-}$ and $m^T_{Br^-}$ are the total molalities of Cl and Br ions in the equilibrium aqueous phase, γ_{Br^-} and γ_{Cl^-} are the activity coefficients of Br^- and Cl^- ions in the equilibrium aqueous phase, σ_{Br} and σ_{Cl} account for ion association by relating total aqueous concentrations to individual ion concentrations (for example $m^T_{Br^-} = (\sigma_{Br} + 1)m_{Br^-}$), χ_{KCl} and χ_{KBr} are the mole fractions of KCl and KBr in the equilibrium solid phase, γ_{KCl} and γ_{KBr} are the activity coefficients of KCl and KBr in the equilibrium solid, and K_{KCl} and K_{KBr} are the solubility products of pure sylvite and pure KBr.

If the solid solution can be considered regular, the following relation can be derived (see Glynn and others, 1991, for application to the NaCl–NaBr–NaOH–H_2O system):

$$\ln D_{Br^-} = \ln\left[\frac{K_{KCl}\gamma_{Br^-}(\sigma_{Cl} + 1)}{K_{KBr}\gamma_{Cl^-}(\sigma_{Br} + 1)}\frac{\exp(a_0\chi^2_{KBr})}{\exp(a_0\chi^2_{KCl})}\right]$$

$$= \ln\left[\frac{K_{KCl}\gamma_{Br^-}(\sigma_{Cl} + 1)}{K_{KBr}\gamma_{Cl^-}(\sigma_{Br} + 1)}\right] - a_0 + 2a_0\chi_{KBr} \qquad (4)$$

or in the case of a subregular solution:

$$\ln D_{Br^-} = \ln\left[\frac{K_{KCl}\gamma_{Br^-}(\sigma_{Cl} + 1)}{K_{KBr}\gamma_{Cl^-}(\sigma_{Br} + 1)}\right] - a_0 + a_1 + (2a_0 - 6a_1)\chi_{KBr} + 6a_1\chi^2_{KBr} \qquad (5)$$

A linear regression of the Durham, Rock, and Frayn (1953) data using eq 4 gives a best fit a_0 value of 1.39 with a standard error of ± 0.04 (see fig. 1). The computed intercept corresponded to a $\gamma_{Br^-}/\gamma_{Cl^-}$ ratio of 1.080. A least squares fit of eq 5 gave the results: $a_0 = 1.37$, $a_1 = -0.16$, $\gamma_{Br^-}/\gamma_{Cl^-} = 1.087$ (see fig. 1).

Extracting a_0 and a_1 data from eqs 4 or 5 relies on the assumption that the ratio of the ion association factors, $((\sigma_{Cl} + 1)/(\sigma_{Br} + 1))$, and the ratio of the aqueous activity coefficients, $\gamma_{Br^-}/\gamma_{Cl^-}$, can be considered constant throughout the range of solid mole fractions investigated. The excellent agreement between the two least squares fits and the a_0 and a_1 values calculated by Glynn and others (1990) and Königsberger and Gamsjäger is due to the relatively small difference between the endmember solubility products ($K_{KCl} = 10^{0.904}$, $K_{KBr} = 10^{1.129}$), which results in a limited range of ionic strengths (4.82–6.14 at the alyotropic maximum) and consequently in a limited range of $\gamma_{Br^-}/\gamma_{Cl^-}$ values (1.075–1.081), very close to the ratios calculated above by linear regression. Furthermore, the KCl–KBr–H_2O system does not have any ion-complexes that have to be taken into account in formulating a Pitzer model of the system. Essentially, the nonidealities of mixing of the KCl, KBr, and H_2O components in the aqueous solutions investigated by Durham, Rock, and Frayn (1953) are small relative to the excess-free-energy of mixing of the solid-solution series.

In the absence of an aqueous thermodynamic model (or in the absence of solid-solution aqueous-solution data), miscibility-gap informa-

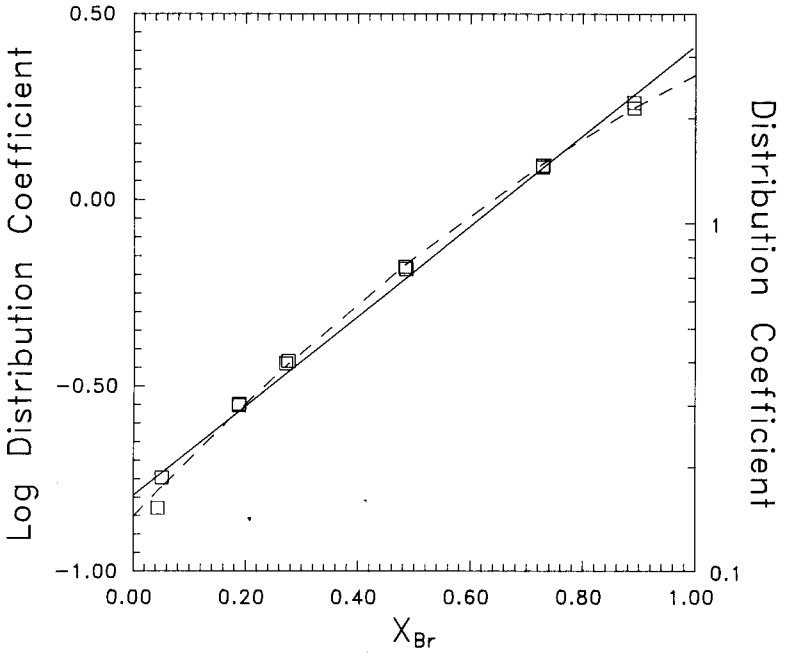

Fig. 1. Linear regression of Durham, Rock, and Frayn (1953) $\log D_{Br^-}$ versus χ_{KBr} results from reversible KCl–KBr–H_2O recrystallisation experiments at 25°C. The solid line is a fit assuming a regular solid-solution model (see eq 4), the dashed line is a fit assuming a subregular model (see eq 5).

tion can also often be used to estimate the thermodynamic-mixing parameters of a solid-solution series. The lack of a miscibility-gap in the KCl–KBr series limits the a_0 parameter to a value smaller than 2 (assuming a regular solution model). Experimental evidence (Busenberg, 1990; unpublished data) of the lack of a miscibility gap at 5°C in the KCl–KBr series can be used to limit the a_0 value at 25°C even further. Given this evidence and the assumption of a strictly-regular solution (for which $S^E = 0$; see Prigogine and Defay, 1954, p. 246, 391), the uppermost value predicted for a_0 at 25°C would be 1.87.

Despite their limitations, the above techniques for estimating excess-free-energy-of-mixing parameters can be used as a first approximation for lack of better data. Glynn (1990, 1991) gives a more complete discussion of these and other estimation techniques.

SUMMARY

1. Königsberger and Gamsjäger's derivation (1987, 1991) relating thermodynamic equilibrium and stoichiometric saturation states by defining them in terms of the total free energy of a solid-solution aqueous-solution system, is an elegant alternative to the derivations presented by Glynn and Reardon (1990) and by Thorstenson and Plummer (1977). Al

these derivations result in similar defining equations and give support to the concept of stoichiometric saturation as a limiting or "constrained" thermodynamic state.

2. By their dependence on aqueous activities of specific ions rather than on elemental aqueous concentrations, Lippmann diagrams incorporate the assumption that the speciation and thermodynamic properties of the aqueous solution can be calculated externally if necessary. As a result, Lippmann diagrams can be applied to a wide variety of aqueous solutions, which may contain many components of insignificant concentration in the solid-solution series investigated. Because they are not based on aqueous mole-fractions and concentrations, Lippmann diagrams are not true analogues of classical binary phase diagrams. By their simplicity, however, Lippmann diagrams may offer valuable insights into the thermodynamics of multicomponent systems.

3. The aqueous thermodynamic model used should always be given when reporting the thermodynamic properties of a solid-solution series determined from solid-solution aqueous-solution reaction data.

4. The concept of "constrained" states for multicomponent solid solutions, in which several, but not all, of the solid-solution components react in stoichiometric proportion to each other, still needs experimental verification. We suggest that the general term "constrained equilibrium" be used to describe the limiting thermodynamic states for multicomponent solids with this reaction behavior. The term "stoichiometric saturation" should be reserved to describe the limiting thermodynamic states for multicomponent solids reacting with a fixed single composition (that is, with *all* solid-solution components constrained to react in stoichiometric proportion to each other).

5. The excess-free-energy parameters determined for KCl-KBr solid solutions by Königsberger and Gamsjäger (1991) and Glynn and others (1990) are in good agreement with both the calorimetric and solubility-derived results reported by Sangster and Pelton (1987) and Kirgintsev and Trushnikova (1963). Despite many assumptions, linear regression fits of the distribution coefficient data of Durham, Rock, and Frayn (1953) are in excellent agreement with the results of Glynn and others (1990) and Königsberger and Gamsjäger.

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