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

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

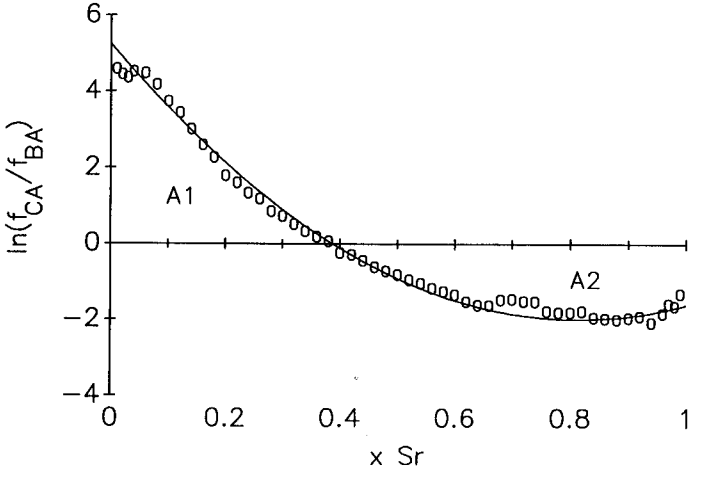

Fig. 1. "Equal-area" test of solid-phase activity coefficient ratios for aragonite–strontianite solid solutions. Solid line was calculated with $G^{E(s)}$ parameters $a_0 = 3.43$ and $a_1 = -1.82$ of eq (19) and satisfies the condition A1 = A2 exactly. Excess parameters and $\partial \log K_{eq}(x)/\partial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

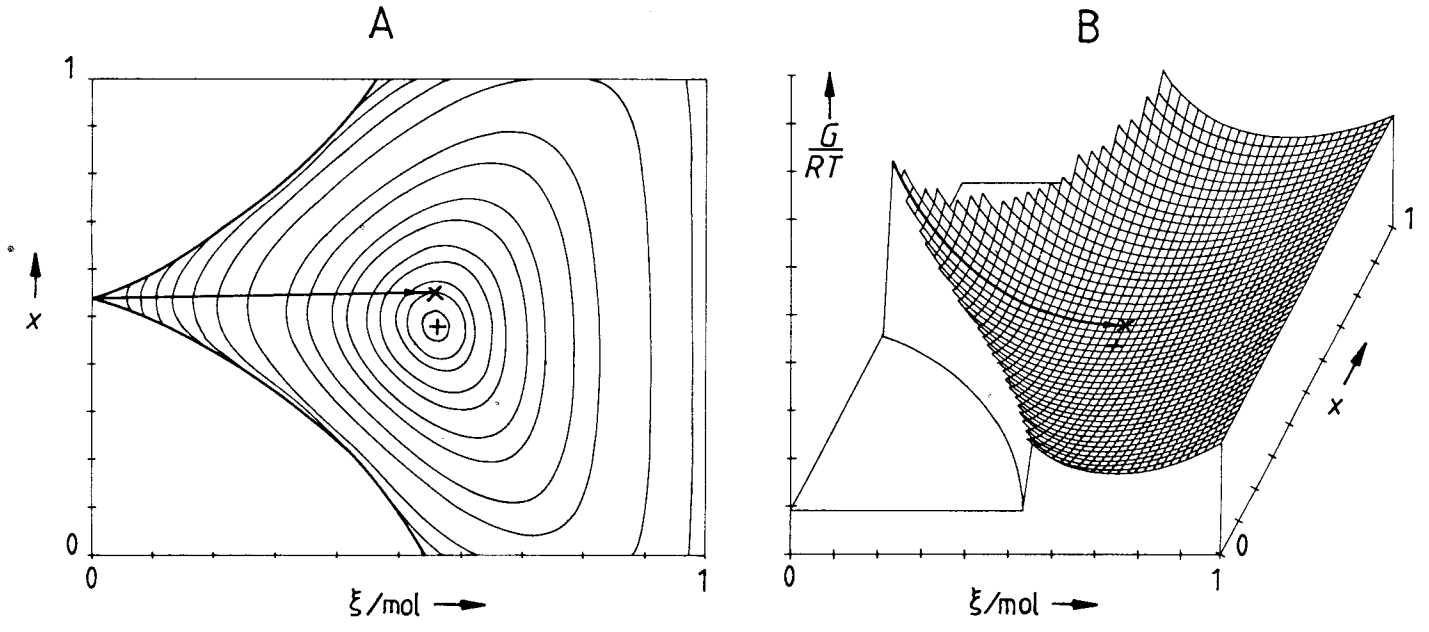

Fig. 2. Contour (A) and axonometric (B) plots of $G(\xi, x)$ for KCl–KBr–H_2 at 25°C. The experimentally observed equilibrium for the initial conditions $x_0 = 0.542$, $n = 1$ mol, and $m = 5.055$ mol (Durham, Rock, and Frayn, 1953, table I, no. 5) corresponds to the absolute minimum of G (+). The hypothetical 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

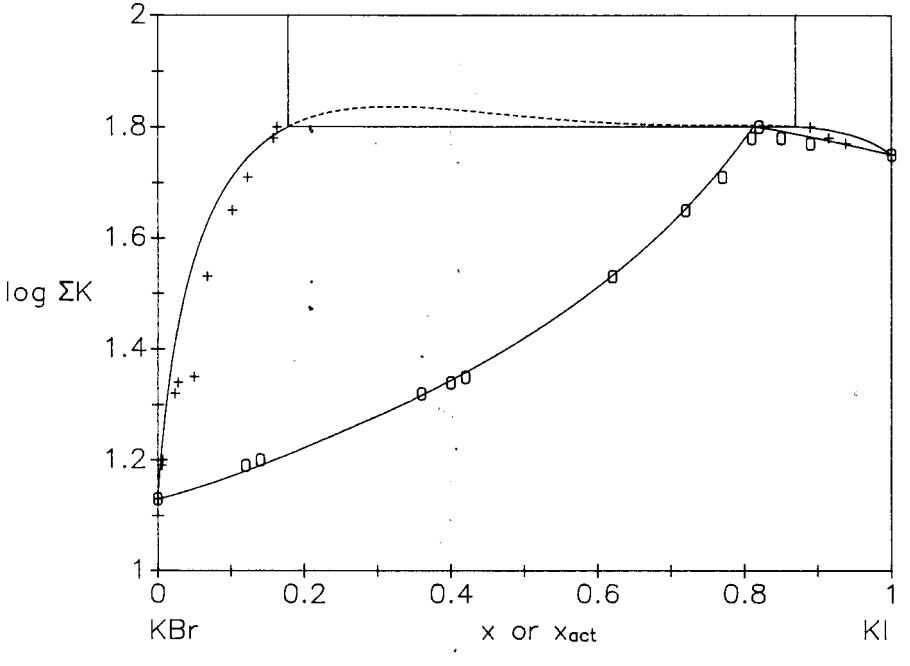

Fig. 3. Lippmann diagram of the system KBr–KI–H_2O at 25°C (solid lines); + solidus, ∘ solutus points (Makarov and Evstrop'ev, 1960). $G^{E(s)}$ parameters of eq (19) are $a_0 = 2.46$ and $a_1 = 0.14$. The solidus inside the miscibility gap (dashed line) is unobservable.

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

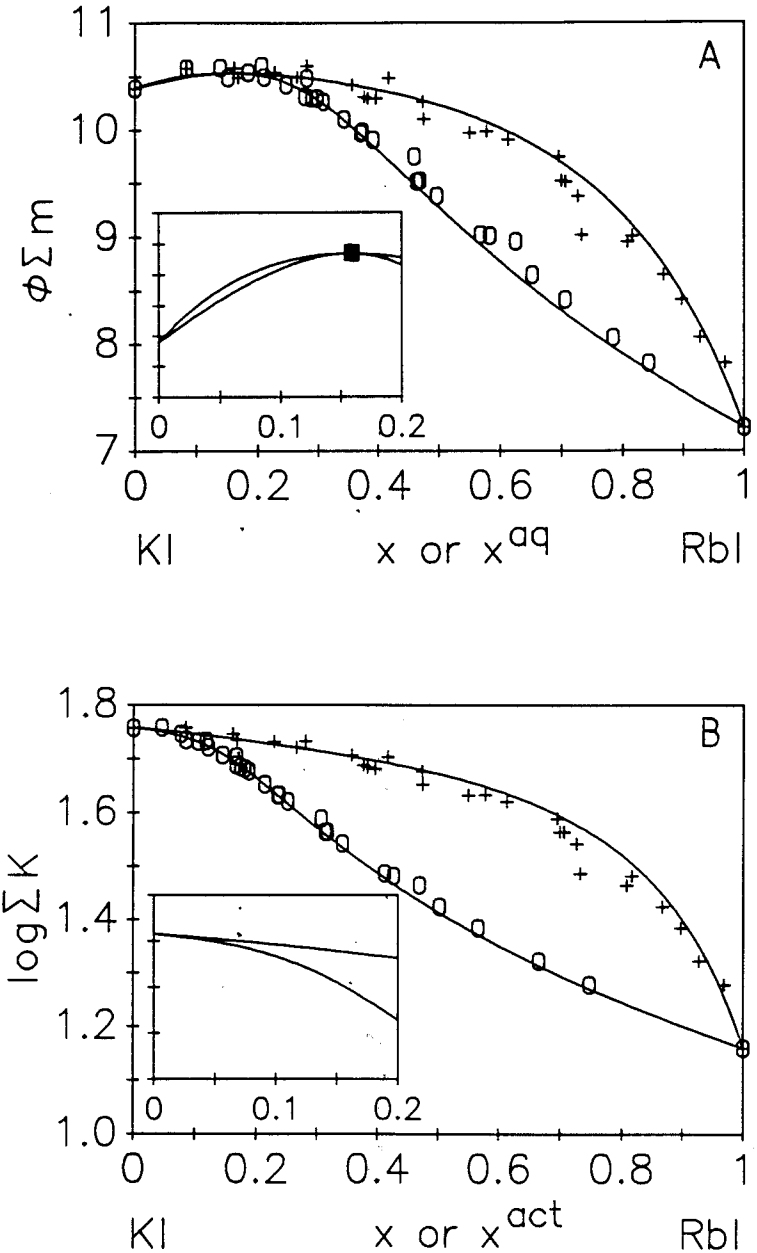

Fig. 4. $\phi\Sigma m$–x–x_{aq} diagram (A) and Lippmann ΣK–x–x_{act} diagram (B) of the system KI–RbI–H_2O at 25°C. + solidus, ∘ solutus points (Makarov and Stupin, 1961). ■ indifferent point. $G^{E(s)}$ parameters of eq (19) are $a_0 = 1.00$ and $a_1 = -0.15$. $G^{E(aq)}$ from Pitzer and Mayorga (1973)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