

## COMMENT

### Comment on "Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems" by P. D. Glynn, E. J. Reardon, L. N. Plummer, and E. Busenberg

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GLYNN et al. (1990) disputed the "assumption" of stoichiometric saturation by STOESEL and CARPENTER (1986) as a control on trace Br contents in precipitation data of halite and sylvite. GLYNN et al. (1990) also disputed the values of limiting activity coefficients of NaBr and KBr in halite and sylvite, respectively, that were predicted by STOESEL and CARPENTER (1986) for trace Br contents in these minerals. There are three parts to this discussion: (1) answering the questions raised by GLYNN et al. (1990) about the general use of stoichiometric saturation as a control on SSAS (solid-solution aqueous-solution) reactions during precipitation; (2) discussing the limiting activity coefficients of NaBr in halite proposed both by STOESEL and CARPENTER (1986) and by GLYNN et al. (1990); and (3) discussing the limitation of a Lippmann phase diagram in determining if a solution composition follows stoichiometric saturation for a trace component in a binary solid solution.

#### STOICHIOMETRIC SATURATION AND PRECIPITATION PROCESSES

GLYNN et al. (1990, p. 275) state there is "no evidence that the concept of stoichiometric saturation can be used in the interpretation of SSAS precipitation processes." Their argument continues that stoichiometric saturation "is a state in which the **solid**, which is of **fixed** composition, controls the composition of the **aqueous** phase, rather than vice versa." They assert that stoichiometric saturation should only be applied to dissolution processes in which the solid phase composition remains constant.

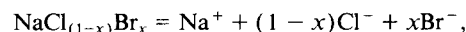
Two problems exist with the restriction on stoichiometric saturation by GLYNN et al. (1990). First, as discussed below, the assumption that the solid-solution composition is constant is not an assumption needed to describe stoichiometric saturation. Indeed, a constant solid-solution composition in a closed system can only be obtained at thermodynamic equilibrium, because a solid solution will always recrystallize in an attempt to reach thermodynamic equilibrium. If taken literally, the constant solid-solution composition assumption by GLYNN et al. (1990) limits the use of stoichiometric saturation to thermodynamic equilibrium.

Second, dissolution of a solid solution is not independent of precipitation. Both processes occur simultaneously on a microscopic level during reaction between a solid solution and an aqueous solution. Indeed, the processes continue to

occur even though the solid solution and aqueous solution stop changing composition, during which the processes of precipitation and dissolution cancel the effects on the compositions of the solutions. If stoichiometric saturation can apply to macroscopic dissolution, which also includes precipitation on a microscopic scale, then logic suggests stoichiometric saturation also applies to macroscopic precipitation which includes dissolution on a microscopic scale.

Stoichiometric saturation occurs when the bulk composition of a solid solution is in equilibrium with an aqueous solution. In the absence of thermodynamic equilibrium, this equilibrium is metastable, producing a constantly changing solid-solution composition in the drive to reach thermodynamic equilibrium. Thermodynamic equilibrium occurs when the end member components within the solid solution are in equilibrium with the aqueous solution. A solid in thermodynamic equilibrium is always in stoichiometric saturation; however, the reverse is not necessarily true.

The following reaction can be written to describe stoichiometric saturation for a binary solid solution of NaBr and NaCl in contact with an aqueous solution:

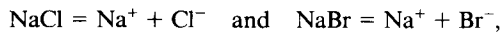


such that

$$\log K_{\text{NaCl}_{(1-x)}\text{Br}_x} = \log a_{\text{Na}^+} + (1-x) \log a_{\text{Cl}^-} + x \log a_{\text{Br}^-}, \quad (1)$$

where  $a_i$  refers to the solution activity,  $x$  is the mole fraction  $X_{\text{NaBr}}$  in the solid solution, and  $K$  is the equilibrium constant of the hydrolysis reaction. The activity of the solid-solution phase is equal to one because that particular composition has been chosen as its standard state. Hence,  $K$  will change with composition of the solid solution and with temperature and pressure. The above equation is the **only** relation that needs to be satisfied at stoichiometric saturation. If the solid-solution composition varies, the aqueous-solution composition can vary to maintain stoichiometric saturation and vice versa.

If thermodynamic equilibrium occurs in the above system, the two solid components NaCl and NaBr (in the solid solution) must be in equilibrium with the aqueous solution. Two hydrolysis reactions provide the constraints (Eqns. 2 and 3) for the solid solution at thermodynamic equilibrium:



such that

$$\log K_{\text{NaCl}} + \log X_{\text{NaCl}} y_{\text{NaCl}} = \log a_{\text{Na}^+} + \log a_{\text{Cl}^-}, \quad (2)$$

and

$$\log K_{\text{NaBr}} + \log X_{\text{NaBr}} y_{\text{NaBr}} = \log a_{\text{Na}^+} + \log a_{\text{Br}^-} \quad (3)$$

where the activity of each solid component has been replaced by the product of its mole fraction  $X$  and its activity coefficient  $y$ .

To relate the conditions of thermodynamic equilibrium to stoichiometric saturation, THORSTENSON and PLUMMER (1977) used only the above three equations plus the Gibbs-Duhem equation. In their derivation, the solid-solution composition is **varied** at thermodynamic equilibrium in order to derive the resulting variation in the log of the hydrolysis equilibrium constant (of the solid solution) with the appropriate aqueous activities. There is no requirement in the use of these equations that the composition of the solid solution remain constant for stoichiometric saturation to occur! For example, stoichiometric saturation must apply at thermodynamic equilibrium, and the solid composition in a solid solution must vary to maintain thermodynamic equilibrium if the associated aqueous solution composition varies.

#### LIMITING ACTIVITY COEFFICIENT OF NaBr IN HALITE

STOESSELL and CARPENTER (1986) predicted trace Br contents in thermodynamic equilibrium in halite as a function of the aqueous solution activity ratios of  $\text{Br}^-:\text{Cl}^-$ . They used the assumption of stoichiometric saturation as the control on amounts of Br incorporated in halite precipitating in laboratory conditions (BRAITSCHE and HERRMANN, 1963). For evaporating seawater at the point of initial halite saturation, the model of STOESSELL and CARPENTER (1986) predicted Br contents of 78 and 27 ppm at 25°C, respectively, for the initial precipitate and one that had recrystallized to thermodynamic equilibrium. These values are in good agreement with the 60 to 75 ppm Br measured for the initial Br content by HERRMANN et al. (1973) from field studies, and the 30 ppm Br calculated for thermodynamic equilibrium from the distribution coefficient measured in slow-growth single crystal experiments at 40°C (LUTZ, 1975).

GLYNN et al. (1990) noted that STOESSELL and CARPENTER (1986) predicted a larger limiting activity coefficient for KBr in sylvite (approximately 8) than was predicted for NaBr in halite (approximately 4). Those activity coefficient values were average values, taken from Fig. 3 of STOESSELL and CARPENTER (1986), for Br mole fractions in the solid solutions ranging from  $10^{-4}$  to  $10^{-3}$ . The actual range was about 3.75 to 4.25 for  $y_{\text{NaBr}}$  and 6 to 12 for  $y_{\text{KBr}}$ . GLYNN et al. (1990) pointed out that the larger ion size of K vs. Na would suggest a smaller activity coefficient for KBr than for NaBr. Yet, the agreement, obtained between predicted Br contents in halite and measured Br contents, supports the value of 4 for the limiting activity coefficient of NaBr. I would suggest the value of 8 for the limiting activity coefficient of KBr in sylvite is too high, as suggested by the decrease in  $y_{\text{KBr}}$  with

decreasing  $X_{\text{NaBr}}$  on Fig. 3 of STOESSELL and CARPENTER (1986).

GLYNN et al. (1990) used an extrapolation of results from KIRGINTSEV and TRUSHNIKOVA (1966, based on the data of SIMONS et al., 1952) to the  $10^{-4}$  mole fraction range, to argue for a limiting activity coefficient of 13 for NaBr at 25°C at trace Br concentrations. However, an important consequence ignored by GLYNN et al. (1990) is the low Br content in halite, predicted from their limiting activity coefficient of NaBr in halite. For example, their value of 13 for  $y_{\text{NaBr}}$  would yield a predicted thermodynamic equilibrium Br content of 9 ppm for halite in equilibrium with evaporating seawater at initial halite saturation. This value was computed using an aqueous activity product for  $(a_{\text{Na}^+})(a_{\text{Br}^-})$  of 0.0809 for evaporating seawater at initial halite saturation (Plummer, pers. commun., 1990, based on the Pitzer equations in the Fortran program PHRPQTIZ) and a log  $K$  of NaBr of 2.97 at 25°C and 1 bar (STOESSELL and CARPENTER, 1986). Nine ppm is more than a factor of 3 below that suggested from the slow-growth single-crystal experiments of LUTZ (1975). Thus, the limiting NaBr activity coefficient in halite from GLYNN et al. (1990) **predicts** a much lower than expected trace Br content in halite at thermodynamic equilibrium with evaporating seawater.

STOESSELL and CARPENTER (1986) stated that "based on the assumption of stoichiometric saturation in precipitation processes, reasonable Br contents in halite could be predicted for thermodynamic equilibrium." GLYNN et al. (1990) can explain the agreement as due to coincidence. However, how can they **explain** the unreasonably low Br contents in halite predicted using their trace activity coefficient?

#### LIPPMANN PHASE DIAGRAMS AND STOICHIOMETRIC SATURATION

GLYNN et al. (1990) used a Lippmann phase diagram for analyzing solid-solution behavior and concluded that it was impossible to determine if the initial aqueous solution states, described by STOESSELL and CARPENTER (1986), were in stoichiometric saturation. As shown below, this conclusion is equally valid for any trace constituent in a binary solid solution.

On a Lippmann phase diagram, the two thermodynamic equilibrium constraints represented by Eqns. (2) and (3) are rewritten into two new equations describing two curves: the "solidus" and the "solutus" curves. For the Na-Cl-Br- $\text{H}_2\text{O}$  system, these curves are given below in Eqns. (4) and (5), in terms of a new variable, the TSP or total solubility product. Equation (4) defines the solidus curve and results from the addition of the left sides of Eqns. (2) and (3). Equation (5) defines the solutus curve and results from the addition of the right sides of Eqns. (2) and (3). The final form of Eqn. (5) was obtained using the constraint that  $X_{\text{NaBr}} + X_{\text{NaCl}} = 1$ , and aqueous activity fractions terms,  $X_{\text{Cl}^-}$  and  $X_{\text{Br}^-}$ , defined by  $X_{\text{Br}^-} = a_{\text{Br}^-}/(a_{\text{Cl}^-} + a_{\text{Br}^-})$  and  $X_{\text{Cl}^-} = a_{\text{Cl}^-}/(a_{\text{Cl}^-} + a_{\text{Br}^-})$ .

$$\text{TSP} = K_{\text{NaCl}} X_{\text{NaCl}} y_{\text{NaCl}} + K_{\text{NaBr}} X_{\text{NaBr}} y_{\text{NaBr}} \quad (4)$$

$$\begin{aligned} \text{TSP} &= a_{\text{Na}^+} a_{\text{Cl}^-} + a_{\text{Na}^+} a_{\text{Br}^-} \\ &= 1/(X_{\text{Cl}^-}/(K_{\text{NaCl}} y_{\text{NaCl}}) + X_{\text{Br}^-}/(K_{\text{NaBr}} y_{\text{NaBr}})). \quad (5) \end{aligned}$$

A Lippmann phase diagram has a TSP ordinate axis and two abscissa axes: a mole fraction of one of the solid components in the binary solid solution, e.g.,  $X_{\text{NaBr}}$ , and the activity fraction of the corresponding ion in aqueous solution, e.g.,  $X_{\text{Br}^-}$ . The solidus curve, from Eqn. (4), is obtained by plotting TSP vs. the solid component mole fraction. The solutus curve, from Eqn. (5), is computed by plotting TSP vs. the aqueous activity fraction of the corresponding aqueous ion. A line parallel to the abscissa on a Lippmann phase diagram will connect two points on the solidus and solutus curves, indicating the compositions of a solid solution and an aqueous solution in thermodynamic equilibrium.

Stoichiometric saturation curves for a **constant** solid-solution composition can be plotted on the Lippmann phase diagram. Equations (1) and (5) are combined to obtain a solutus curve for stoichiometric saturation.

$$\text{TSP} = K_{\text{NaCl}_{1-x}\text{Br}_x} / [(X_{\text{Cl}^-}^{1-x})(X_{\text{Br}^-}^x)]. \quad (6)$$

The intersection of the solutus curves computed from Eqns. (5) and (6) marks the aqueous-solution composition at which a particular solid-solution composition in stoichiometric saturation is also in thermodynamic equilibrium. A line drawn parallel to the abscissa should intersect the solidus curve with the identical solid-solution composition.

The Lippmann phase diagram approach is not useful for a trace component such as NaBr in halite. The solidus and solutus curves are dominated by the major component NaCl and become equivalent to the curves for pure halite. The curve for stoichiometric saturation for trace composition of NaBr reduces to the solutus curve for pure halite. As  $X_{\text{Br}^-} \Rightarrow$  zero, Eqn. (6) reduces to  $\text{TSP} = K_{\text{NaCl}_{1-x}\text{Br}_x}$ , since both  $X_{\text{Cl}^-}^{1-x}$  and  $X_{\text{Br}^-}^x$  approach unity. The latter approaches unity because  $x \Rightarrow 0$ . Equation (6) eventually becomes  $\text{TSP} = K_{\text{NaCl}}$ , because the limiting value of the equilibrium constant for the solid solution is that of the pure solid as  $X_{\text{NaBr}}$  goes to zero.

### CONCLUSIONS

1) Stoichiometric saturation does not require a mineral to react with a constant composition. Hence, the concept may be applied both to dissolution and precipitation processes.

- 2) The activity coefficient of NaBr predicted by STOESEL and CARPENTER (1986) is reasonable; whereas, the value predicted by GLYNN et al. (1990) is not reasonable.
- 3) Solid-solution and aqueous-solution compositions plotted on a Lippmann phase diagram are of limited use in the region of a trace component in a binary solid solution. The data fall on or near curves describing the pure solid (without the trace component), obscuring the distinction between stoichiometric saturation and thermodynamic equilibrium.

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