

ACCURATE P-T-X-V-H CORRELATIONS FOR THE SYSTEM NaCl-H₂O FROM 0 TO 800°C, 0 TO 500 MPa, AND 0 TO 1 X_{NaCl}

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A set of simple correlation formulae for the phase boundaries in P-T-X space, and for the volumetric properties of liquid, vapour, supercritical fluid as well as solid and liquid NaCl as a function of temperature, pressure and composition have been developed. We consider the formulae accurate within experimental error from 0 to 800°C, 0 to 500 MPa, and 0 to 1 X_{NaCl}. Phase boundaries (critical curve, liquid+vapour coexistence surface, halite melting and boiling curves, halite+liquid+vapour coexistence, and halite liquidus) were fitted with simple formulae. The pure water side is described by the equation of state of HAAR et al. (1984).

The formulae are based on essentially all experimental data available in the literature, which have carefully been re-examined. Many apparent discrepancies between different studies could be resolved and are mostly due to improper treatment of the raw experimental data. For example, the scatter of composition and density values along the critical curve could substantially be reduced (DRIESNER AND HEINRICH, 2002). We found that only the critical data from the synthetic fluid inclusion study of KNIGHT and BODNAR (1989) substantially deviate from our best-fit line. This most likely results from extrapolation uncertainties of the equation of state used in their study and to a lesser degree from the effect that apparent "critical homogenisation" in the two-component system may occur over a range of temperatures for a given composition but at different densities.

For fitting the volumetric properties, densities were converted to molar volumes V_M based on the components NaCl and H₂O. This conversion substantially simplified the dependency on P, T, and X. For example, the shape of the halite liquidus (Fig. 1) requires a rather complex fitting formula in T-r space while in T- V_M space it could be fitted as isobars by a simple quadratic polynomial $V_{M,Liquidus} = a_0 + a_1T + a_2T^2$, and extrapolates well to the molar volume of liquid NaCl at the halite melting curve.

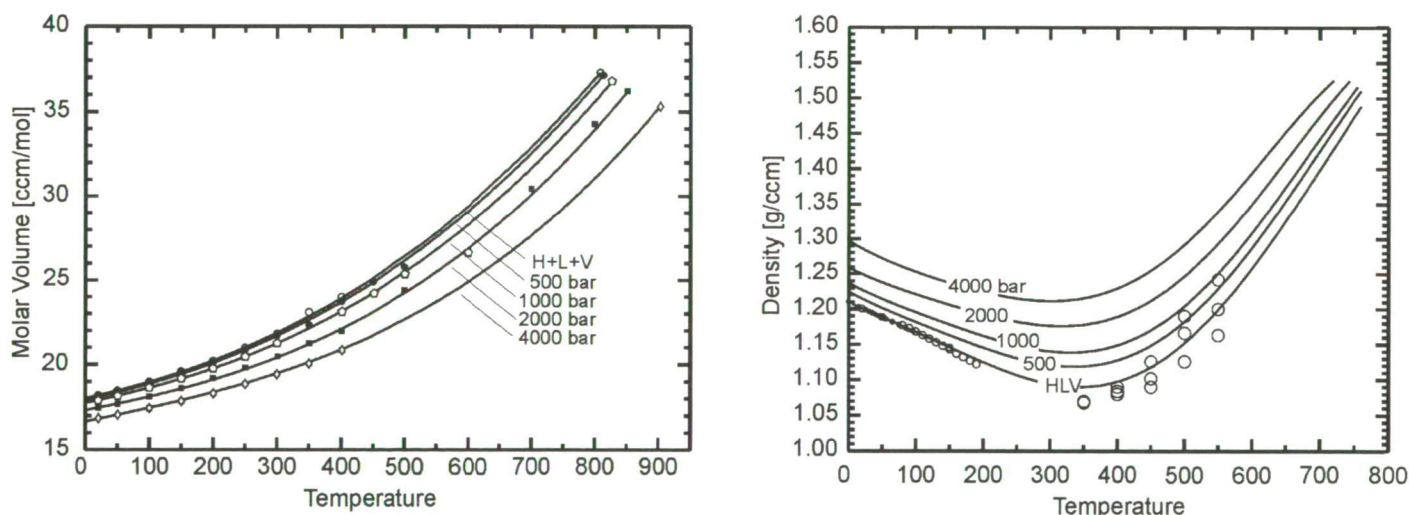


Fig. 1: Halite liquidus at Halite+Liquid+Vapour coexistence pressure and four isobars.

While the position of the liquidus is well known in P-T-X space, the volumetric properties of the halite-saturated brine are poorly known at best (large circles in Fig. 1, right side: estimates from (CHOU, 1987), for the brine density along the H+L+V surface). Improved values (symbols in left graph of Fig. 1) were obtained in an iterative procedure by fitting various equations to experimental data of mixed H₂O-NaCl fluids (e.g. (HILBERT, 1979; URUSOVA, 1975)) and extrapolating to X_{NaCl} at halite saturation. Simple, four-parameter equations $V_{M,fluid} = b_0 + b_1 * X + b_2(b_3 + X)^c$ (c being a constant) were found to be sufficient to fit all experimental volumetric data for mixed H₂O-NaCl fluids as isotherms-isobars over the whole range with only minor uncertainties even in the critical region. The extrapolated values for the halite liquidus values turned out to be very robust (+/- 0.5%) and largely independent of the choice of c . Three of the four parameters are constrained by the known molar volume of water, the partial molar volume of NaCl, and the halite liquidus volume. The fourth parameter of the volume equation for H₂O

–NaCl shows a simple dependency on temperature and pure water density. The volume formula was integrated to obtain enthalpy data, which were then fitted by simple correlation formulae as well.

We currently implement the correlations into our finite-element, finite-volume fluid flow code CSP in order to simulate the hydrology of saline fluids around magmatic bodies, including the simultaneous flow of both brine and vapour phases. Computer programs for fluid inclusion studies are in preparation.

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