The System H₂O-NaCl

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The system H₂O-NaCl represents the most important fluid system for interpretation of fluid inclusion microthermometric data. Salinities of aqueous inclusions are almost always calculated on an NaCl-equivalent basis using the measured freezing-point depression or halite dissolution temperatures, even when other information suggests that the inclusion is not represented by the pure H₂O-NaCl system. Similarly, isochores for virtually all non-gas-bearing aqueous inclusions are approximated using PVT data for the H₂O-NaCl system.

Although the H₂O-NaCl system is one of the most studied aqueous systems, large gaps still exist in the PTX database needed to interpret fluid inclusion measurements. In recent years, much progress has been made towards filling those gaps. Research currently underway in our lab is directed towards developing a complete set of internally consistent PTX data for the system H₂O-NaCl and incorporating these data into a computer algorithm for interpretation of fluid inclusion microthermometric data.

Numerous experimental studies of the volumetric properties of H₂O-NaCl have been published. However, each of these covers only a limited portion of PVTX space, and there is often poor agreement where various studies overlap. A major project is currently underway to evaluate the available data and to fill in gaps where data do not exist, and to develop a comprehensive algorithm which may be used to model H₂O-NaCl fluid inclusions. Therefore, PVT data for H₂O-NaCl will not be considered in this review as much of the data and equations will be outdated soon after publication of the present survey.

PHASE EQUILIBRIUM DATA

Freezing-Point Depression

The most recent and complete data for the freezing-point depression of H₂O-NaCl solutions is that of Hall et al. (1988). Their experimental data have been regressed to obtain a simple polynomial equation relating the salinity and freezing-point depression according to:

$$\text{Salinity (wt.\%)} = 0.00 + 1.78 \theta - 0.0442 \theta^2 + 0.000557 \theta^3 \quad (1)$$

where θ is the depression of the freezing point in degrees Celsius. Equation (1) reproduces the original experimental data of Hall et al. to better than ± 0.05 wt.% NaCl at all temperatures from 0.0°C to -23.21°C, the eutectic temperature for H₂O-NaCl. The data of Hall et al. (1988) and equation (1) above also provide a more accurate description of the relationship between salinity and freezing-point depression than the earlier equations of Potter et al. (1978), particularly at salinities above about 15 wt.%. A detailed comparison of salinities predicted by equation (1) and the equation of Potter et al (1978) is discussed by Bodnar (1992a)

Halite Solubility (vapor-saturated)

The solubility of halite along the vapor-saturation surface has been determined by Sterner et al. (1989). Their equation (4), reproduced here as equation (2), may be used to calculate fluid inclusion salinities for halite dissolution temperatures from 0.1° to 801°C:

$$\begin{aligned} \text{Salinity (wt.\%)} = & 26.242 + 0.4928 \Psi + 1.42 \Psi^2 - 0.223 \Psi^3 + 0.04129 \Psi^4 \\ & + 6.295 \times 10^{-3} \Psi^5 - 1.967 \times 10^{-3} \Psi^6 + 1.1112 \times 10^{-4} \Psi^7 \end{aligned} \quad (2)$$

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where $\Psi = T(^{\circ}\text{C})/100$. Note that equation (2) is valid only for fluid inclusions in which the halite dissolves at a temperature less than or equal to the vapor disappearance temperature. For inclusions in which halite is the final phase to disappear, solubility data along the liquidus must be used to calculate solubilities as described below.

Halite Solubility (liquidus)

The pressure coefficient of halite solubility, i.e., the liquidus in the H_2O -NaCl system, has recently been studied by several workers using various experimental techniques. Gunter et al. (1983) determined a slope for the NaCl liquidus of $24^{\circ}\text{C}/\text{kbar}$ and found that the slope became steeper ($\Delta T/\Delta P$ decreases) with decreasing salinity. The data of Gunter et al. (1983) have been combined with the recent data of Bodnar (1992b), which extends the salinity range down to 40 wt.% NaCl. These combined data indicate that the slope of the liquidus decreases by $0.474^{\circ}\text{C}/\text{wt.}\% \text{ NaCl}$. The slope changes from positive to negative at a salinity of ~ 49.5 wt.% NaCl. Thus, if an inclusion homogenizes by halite dissolution and if the salinity of the inclusion is calculated using vapor-saturated solubility data (equation (2) above), the calculated salinity will be a minimum if $T_m(\text{NaCl})$ is less than about 425°C . $T_m(\text{NaCl})$ above 425°C will provide a maximum salinity, and $T_m(\text{NaCl})$ of approximately 425°C will provide the correct salinity regardless of the mode of homogenization because the solubility of NaCl at this composition is essentially independent of pressure. The interpretation of fluid inclusions which homogenize along the liquidus, and the implications for both salinity and isochore determinations is discussed by Bodnar (1992b).

Vapor Pressure

The vapor pressure in a fluid inclusion at homogenization is needed in order to define the starting point for extrapolating the fluid inclusion isochore to higher P-T conditions to determine formation conditions. Experimental studies of the vapor pressure of H_2O -NaCl solutions include those of Keevil (1942), Sourirajan and Kennedy (1962), Khaibullin and Borisov (1966) and Bodnar et al. (1985). Bodnar (unpublished data) has developed the following two equations to calculate vapor pressures along the three phase curve (liquid + vapor + solid):

$$P = \exp [-5.38 + 0.0688 T - 2.08 \times 10^{-4} T^2 + 2.96 \times 10^{-7} T^3] \quad (3)$$

where P is the pressure in bars and T is the temperature in degrees Celsius. Equation (3) is valid from the eutectic temperature (-21.2°C) to 180°C . Note that from -21.2°C to 0.1°C the stable solid phase along the three phase curve is hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). From 180°C to 800°C the pressure along the three phase curve is given by:

$$P = -135.99 + 304.37 \Psi - 236.18 \Psi^2 + 78.625 \Psi^3 - 10.094 \Psi^4 + 0.4244 \Psi^5 \quad (4)$$

where $\Psi = T(^{\circ}\text{C})/100$ and P is the pressure in bars.

Critical Point

The critical properties of H_2O -NaCl solutions have been determined by numerous workers. The most recent and complete study is that of Knight and Bodnar (1989) who determined the critical temperatures, pressures and densities for compositions from 0-30 wt.% NaCl using synthetic fluid inclusions. The critical temperature and pressure are given by:

$$T_c = 374.1 + 8.800 \phi + 0.1771 \phi^2 - 0.0211 \phi^3 + 7.334 \times 10^{-4} \phi^4 \quad (5)$$

$$P_c = 2094 - 20.56 T_c + 0.06896 T_c^2 - 8.903 \times 10^{-5} T_c^3 + 4.214 \times 10^{-8} T_c^4 \quad (6)$$

where T_c and P_c are the critical temperature ($^{\circ}\text{C}$) and pressure (bars), respectively, and ϕ is the salinity in weight percent NaCl.

Liquid-Vapor Equilibria

The three most extensive experimental studies of liquid-vapor equilibria in the H_2O -NaCl system are those of Khaibullin and Borisov (1966), Sourirajan and Kennedy (1962) and Bodnar et al. (1985). Khaibullin and Borisov determined the composition of the vapor in equilibrium with liquids over the range 100° - 440°C for liquid compositions up to 25 wt.% NaCl. Sourirajan and Kennedy (1962) determined the liquid and vapor compositions from 350° - 700°C for salinities ≤ 26.4 wt. % NaCl. Bodnar et al (1985) determined the compositions of coexisting liquid and vapor from 550° - 1000°C . Numerous other experimental studies of liquid-vapor equilibria over limited PTX ranges have been conducted (c.f., Copeland et al., 1953) and several workers have developed empirical to semi-theoretical equations to describe the PTX properties over small PTX ranges (cf., Bischoff, 1991).

At the present time, sufficient experimental data do not exist to develop a comprehensive algorithm to describe the PTX properties of liquids and vapors in the two-phase region of the H_2O -NaCl system over the complete range of conditions of interest to inclusionists. Work is currently underway in our laboratory to collect data needed to completely describe liquid-vapor equilibria in the H_2O -NaCl system. These data will be combined with available information to develop a computer model to describe PVTX properties of H_2O -NaCl.

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