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Extending from Dilute Range to the Fused Salt — Evaluation
of Parameters to High Temperatures and Pressures**

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ABSTRACT

Models based on general equations for the excess Gibbs energy of the aqueous fluid provide thermodynamically consistent structures for evaluating and predicting aqueous electrolyte properties. These equations yield other quantities upon appropriate differentiation, including osmotic and activity coefficients, excess enthalpies, heat capacities, and volumes. For this reason a wide array of experimental data are available from which model parameters and their temperature or pressure dependence can be evaluated. For systems of moderate concentration, the most commonly used model at present is the ion-interaction approach developed by Pitzer (1) and coworkers. For more concentrated solutions, including those extending to the fused salt, an alternate model based on a Margules-expansion and commonly used for nonelectrolytes was proposed by Pitzer and Simonson (40). We discuss these two models and give examples of parameter evaluations for some geologically relevant systems to high temperatures and pressures; also we show applications of the models to calculations of solubility equilibria.

INTRODUCTION

Attempts to understand various geochemical processes, including those related to hydrothermal brines, seawater systems, and evaporite formation, as well as industrial problems, such as corrosion and scaling in geothermal systems, power plants, and cooling systems of nuclear reactors, require a thorough knowledge of the thermodynamic properties of aqueous electrolyte solutions. Essential to these are chemical models that accurately describe the excess properties of aqueous electrolytes over wide ranges of temperature, pressure, and concentration, and which allow prediction of these properties for complex mixtures based on parameters evaluated from simple systems. Chemical models based on general equations for the excess Gibbs energy of the aqueous solution provide thermodynamically consistent structures for the evaluation and prediction of aqueous electrolyte properties. These equations yield other quantities upon appropriate differentiation, including osmotic and activity coefficients, excess enthalpies, entropies, heat capacities, and volumes. For this reason, a wide array of experimental techniques provide data from which model parameters and their temperature or pressure dependence can be evaluated.

The purpose of this paper is to review two thermodynamic models for aqueous electrolyte solutions and to give examples of parameter evaluations to high temperatures and pressures, as well as applications to solubility calculations. The first model has been discussed extensively elsewhere (1-4) and will be reviewed only briefly here, while more detail will be given for the second model.

In both models the Gibbs energy of the solution is written as the sum of an ideal term and an excess term

$$G = G^{id} + G^{ex}, \quad (1)$$

but the measure of composition and the forms of the ideal as well as the excess terms are different. In one case the measure of composition is molality, i.e. moles of solute species per kg. of solvent, and the ideal activity is taken to be proportional to the molality. This leads to the following expression for the ideal Gibbs energy:

$$G^{\text{id,m}} = n_w \mu_w^\circ + \sum_i n_i [\mu_i^{\circ\text{m}} - RT(1 - \ln m_i)], \quad (2)$$

where the superscript m indicates the molality basis, μ_w° and $\mu_i^{\circ\text{m}}$ are the standard state chemical potentials of water and solute species i, respectively, and n_i and m_i are the number of moles and the molality of species i, respectively. Then activities, activity coefficients (γ_i^{m}), and the osmotic coefficient are related by

$$a_i = m_i \gamma_i^{\text{m}} \quad (3)$$

$$\phi = -(\Omega / \sum_i m_i) \ln a_w \quad (4)$$

with Ω the number of moles of solvent per kg. (55.51 for water) and the sum covers all solute species. Also,

$$G^{\text{ex,m}}/w_w RT = \sum_i m_i (1 - \phi + \ln \gamma_i^{\text{m}}) \quad (5)$$

where w_w is the number of kg. of solvent. The molality system is in general use for aqueous solutions of moderate concentration, but it becomes unsatisfactory at very high solute concentrations. Indeed the molality becomes infinite for a pure fused salt.

The alternate system uses mole fraction as a measure of composition; it is used generally for nonionic solutions and can be symmetrical with regard to the various components. In this system the ideal Gibbs energy is

$$G^{\text{id,x}} = \sum_i n_i (\mu_i^{\circ\text{x}} + RT \ln x_i), \quad (6)$$

with x_i the mole fraction of species i and the superscript x indicates the mole fraction system. Now $\mu_i^{\circ\text{x}}$ is either the chemical potential of the pure liquid i, or an extrapolated value at infinite dilution:

$$\mu_1^{\circ X} = \lim_{x_1 \rightarrow 0} (\mu_1 - RT \ln x_1). \quad (7)$$

For the infinite dilution case, however, $\mu_1^{\circ X}$ differs from $\mu_1^{\circ m}$ because of the difference between $\ln x_1$ and $\ln m_1$; specifically, $\mu_1^{\circ m} - \mu_1^{\circ X} = RT \ln \Omega$.

The excess Gibbs energy in the mole fraction system is

$$G^{ex,X} = RT \sum_i n_i \ln \gamma_i^X \quad (8)$$

where γ_i^X is the activity coefficient in this system.

ION-INTERACTION OR VIRIAL COEFFICIENT APPROACH

For systems ranging from dilute to moderate concentrations, the most commonly used model at present is based on a virial expansion developed by Pitzer (1). For a system with one solute, MX, having ν_M cations of charge z_M and ν_X anions of charge z_X , the excess Gibbs energy can be written as

$$G^{ex}/n_w RT = f(I) + 2\nu_M \nu_X [m^2 B_{MX}(I) + m^3 \nu_M z_M C_{MX}] \quad (9a)$$

where n_w is the number of kilograms of solvent, $f(I)$ is a Debye-Hückel function, m is the molality and I is the ionic strength. B_{MX} and C_{MX} are, respectively, second and third virial coefficients representing short-range interactions between ions taken two and three at a time, and which can be determined from experimental data on single electrolyte solutions. Two additional virial coefficients, ϕ and ψ , arise for ternary and more complex systems, but these can be evaluated from data on simple mixtures (2-5). The ionic strength of $B_{MX}(I)$ is given by

$$B_{MX} = B_{MX}^{(0)} + B_{MX}^{(1)} g(\alpha_1 I^{1/2}) + B_{MX}^{(2)} g(\alpha_2 I^{1/2}) \quad (9b)$$

where

$$g(x) = 2[1 - (1+x)\exp(-x)]/x^2. \quad (9c)$$

From basic thermodynamics, the excess Gibbs energy can be related to other solution properties. Equation (9) for the excess Gibbs energy then yields, upon appropriate differentiation, Eqns. (10)-(15) given in Table 1 for osmotic and activity coefficients, apparent molal enthalpy, heat capacity, and

volume. The ion-interaction parameters $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX} in Eqns. (9), (10), and (11) for the Gibbs energy, osmotic coefficient and activity coefficient, respectively, are specific to each solute, MX, and are functions of temperature and pressure. Because geochemical and industrial processes occur over wide ranges of temperature and pressure, a knowledge of the T and P dependence of these parameters is particularly important. It is essential to understand, therefore, that the temperature dependence of $\beta_{MX}^{(i)}$ and C_{MX} are related to the parameters for the excess enthalpies ($\beta_{MX}^{(i)L}$, C_{MX}^L) and heat capacities ($\beta_{MX}^{(i)J}$, C_{MX}^J) as given in Eqns. (12) and (13). Their pressure dependence, on the other hand, are related to the parameters for the volume as given in Eqn. (14).

Thus the model parameters and their temperature and pressure functions can be evaluated from a wide array of experimental data extending upward in temperature and pressure. At high temperatures, while vapor pressures as well as isopiestic measurements have provided the bulk of available data on activity and osmotic coefficients, recent developments in flow-calorimetry have enabled precise measurements of excess enthalpies and heat capacities of aqueous electrolytes to 300°C or higher (6-13). Flow measurements have also recently been successful in providing precise volumetric data on electrolyte solutions to high temperatures and pressures (14). Evaluation of these new data using the ion-interaction model and the relationships between the various parameters as shown by Eqns. (12) to (14) then yield values of osmotic and activity coefficients, as well as other quantities of interest, at various temperatures and pressures.

In the case of systems for which a variety of experimental methods have been used, it is advantageous to develop general equations based on all critically evaluated data. Examples are the equations for the thermodynamic

properties of NaCl(aq) to 300°C and 1 kb (15,16), of KCl(aq) to 325°C and 500 bars (12), of the alkali chlorides to 250°C at saturation pressure (17), and of the alkali sulfates to 225°C at saturation pressure (18). In some cases experimental data on electrolyte activity at high temperatures are limited and parameter evaluations have to rely on other types of measurements. A good example is Na₂SO₄(aq) for which a chemical model was developed by Holmes and Mesmer (18) from their isopiestic measurements to 225°C and other literature data. Our solubility calculations (19), however, indicated that their model can be improved by additional experiments at temperatures above 180°C. These were provided by our heat capacity measurements (13) from 140 - 300°C at a pressure of 200 bars. We fit our data to Eqn. (13) to yield $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, and C_{MX}^J , as well as standard state heat capacity, $\bar{C}_{p, MX}^{\circ}$, at various temperatures. There are no theoretically-based functions to express the isobaric temperature dependence of each parameter, but a useful form for temperatures 0-350°C is given by

$$f(T) = q_1 + q_2 \ln T + q_3/T + q_4 T + q_5 T^2 + q_6/(T-227) + q_7/(647-T) \quad (16)$$

where 227 K is a temperature in the vicinity of which supercooled water exhibits a singularity (20), and 647 K approximates the critical temperature of pure water. The last two terms in Eqn. (16) have been found useful to represent the extreme behaviour of apparent molal properties as these temperatures are approached (12,13,15,16,21). Because of covariances between model parameters, and also due to the varying quality of experimental data in different P and T regions, not all terms in Eqn. (16) for each ion-interaction parameter are usually needed to represent the data within experimental uncertainty, but elimination of unnecessary parameters is by trial and error. Our derived model for Na₂SO₄(aq) properties from 25-300°C was also based on other types of data, but above 200°C, values for osmotic and activity

coefficients are determined mostly by the second integrals of the temperature functions for $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, and C_{MX}^J evaluated from our heat capacity measurements. Also, in this particular case, the pressure dependence of the thermodynamic properties of $\text{Na}_2\text{SO}_4(\text{aq})$ were estimated from those of $\text{NaCl}(\text{aq})$ determined by Rogers and Pitzer (15). Details of the parameter evaluations for $\text{Na}_2\text{SO}_4(\text{aq})$ are described in Pabalan and Pitzer (13), and applications of the derived model to solubility calculations are given below.

An important use of chemical models for electrolyte solutions, as well as a stringent test of equations for activity and osmotic coefficients, is the prediction of mineral solubilities in electrolyte mixtures. Recent studies have shown that the ion-interaction model can be used successfully to predict solubility equilibria to high temperatures (13,19,22). In the examples given below, solubilities of sodium sulfate minerals, which have four stable forms from 0°C to the melting point, are calculated and compared with experimental values. $\text{Na}_2\text{SO}_4(\text{aq})$ activity and osmotic coefficients, as well as standard state Gibbs energies, were calculated from our model (13), while Gibbs energies of the solids were taken from the literature (23,24). In Fig. 1, predicted solubilities of sodium sulfate solids in water to 350°C are compared to experimental values tabulated by Linke (25). While the calculated values are higher than the experimental data below 241°C, the differences are not large, averaging 0.08 m Na_2SO_4 .

For solubility calculations in ternary and more complex systems, the ion-interaction model requires two additional terms, ϕ and ψ (5). While both these parameters undoubtedly vary with temperature, for solubility calculations we have found it adequate to keep ϕ at its 25°C value and to assign simple temperature functions to ψ (13,19). For the ternary systems $\text{Na}_2\text{SO}_4\text{-NaCl-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$, calculated solubilities up to 300°C are

compared with experimental values (25,26) in Figs. 2 and 3, respectively. More stringent tests of the model are solubility calculations in the quaternary system $\text{Na}_2\text{SO}_4\text{-NaCl-NaOH-H}_2\text{O}$, for which predicted and experimental solubilities at 200° and 300°C are compared in Fig. 4. Other examples of solubility calculations using the ion-interaction approach are given in 4, 19, 22, and 27-35.

MARGULES-EXPANSION MODEL

We now turn our attention to systems which may range in concentration from dilute solutions to the fused salt. While aqueous solutions miscible over the whole concentration range at moderate temperatures are relatively uncommon, there are electrolytes of geochemical and industrial interest which become extremely soluble in water at high temperatures and pressures. Although the ion-interaction model can represent electrolyte properties to very high ionic strengths by using additional virial terms (36), this treatment becomes more complex and unsatisfactory at sufficiently high concentration. In addition, for a pure fused salt the molality is infinite. Thus an alternate model is required for systems extending to the fused salt and for other systems of very high but limited solubility.

The model discussed below is analogous to those used for nonelectrolyte solutions. Various expressions have been used to describe the excess Gibbs energy of nonelectrolytes (37), and the Margules expansion has been used successfully by Adler et al. (38) on several nonelectrolyte systems. The theoretical basis for using this approach on electrolyte solutions was discussed by Pitzer (39). Briefly, in concentrated electrolyte solutions the substantial ionic concentration effectively screens the long-range interionic forces to short-range. Thus all of the interparticle forces are effectively short-range and the properties of the system can be calculated by methods

similar to those for nonelectrolytes. In the dilute range, however, where ionic concentrations are very low, the screening effect is lost and the long-range nature of electrostatic forces must be considered. As with the ion-interaction model, this effect is described by an extended Debye-Hückel treatment.

The Gibbs energy per mole is given by the sum of terms for short-range and electrical effects:

$$G^{\text{ex},x}/\sum_1 n_1 = g^{\text{ex}} = g^{\text{s}} + g^{\text{DH}}. \quad (17)$$

A choice must be made for the reference state for the solute: either the pure liquid (possibly supercooled), or the solute at infinite dilution in the solvent. The latter differs from the conventional solute standard state only in the use of mole fraction instead of molality units. For the activity coefficient of a symmetrical salt MX, one has either

$$\ln (\gamma_M^x \gamma_X^x) \rightarrow 0 \text{ as } x_1 \rightarrow 0 \quad (18)$$

$$\ln (\gamma_M^* \gamma_X^*) \rightarrow 0 \text{ as } x_1 \rightarrow 1, \quad (19)$$

where the symbol * denotes the infinitely dilute reference state on a mole fraction basis, and x_1 is the mole fraction of the solvent on an ionized basis, i.e.,

$$x_1 = n_1 / (n_1 + 2n_2) \quad (20)$$

with n_1 and n_2 the numbers of moles of solvent and solute, respectively. We define, also, the mole fractions

$$x_M = x_X = n_2 / (n_1 + 2n_2) = (1 - x_1) / 2 \quad (21)$$

$$x_2 = x_M + x_X = 1 - x_1 \quad (22)$$

and the ionic strength on a mole fraction basis

$$I_x = (1/2) \sum_1 x_i z_i^2 \quad (23)$$

with z_i the charge on the i th ion. For the present case with $z = 1$, $I_x = x_2/2$.

This system of equations for electrolytes was developed in detail for singly-charged ions by Pitzer and Simonson (40). While they considered both types of reference state for the solute, most of their working equations are for the pure liquid reference state. This basis was used for NaCl-H₂O by Pitzer and Li (41) for a study extending to 550°C. For the present research limited to 350°C, however, it seemed better to use the infinitely dilute reference state, and the following equations are derived on that basis:

$$g^S/RT = -x_2^2(W_{1,MX} - x_1U_{1,MX}) \quad (24)$$

where $W_{1,MX}$ and $U_{1,MX}$ are specific to each solute MX and are functions of temperature and pressure. For the Debye-Hückel term representing the long-range electrostatic contribution, one has

$$g^{DH}/RT = -(4A_X I_X / \rho) \ln(1 + \rho I_X^{1/2}). \quad (25)$$

The Debye-Hückel parameter A_X is related to the usual parameter A_ϕ (for the osmotic coefficient on a molality basis) by

$$A_X = \Omega^{1/2} A_\phi. \quad (26)$$

Appropriate differentiations of the Gibbs energy with respect to the numbers of moles of 1 and MX (at constant T and P) yield the equations for the activity coefficients:

$$\ln \gamma_1 = 2A_X I_X^{3/2} / (1 + \rho I_X^{1/2}) + x_2^2 [W_{1,MX} + (1 - 2x_1)U_{1,MX}], \quad (27)$$

$$\begin{aligned} \ln (\gamma_M^* \gamma_X^*) = & -2A_X \{ (2/\rho) \ln(1 + \rho I_X^{1/2}) + I_X^{1/2} (1 - 2I_X) / (1 + \rho I_X^{1/2}) \} \\ & + 2(x_1^2 - 1)W_{1,MX} + 4x_2 x_1^2 U_{1,MX}. \end{aligned} \quad (28)$$

The activities of the solvent and the solute are then given by

$$\ln a_1 = \ln(x_1 \gamma_1), \quad (29)$$

$$\ln a_{MX} = \ln(x_M x_X \gamma_M^* \gamma_X^*). \quad (30)$$

The parameter ρ in Eqns. (24), (25), (27), and (28) is related to the distance of closest approach of ions. To keep the equations for the thermodynamic properties of electrolyte mixtures simple, it is desirable to

have the same value of ρ for a wide variety of salts and for a wide range of temperature and pressure. For the systems considered in this study, a constant value of 15.0 was found to be satisfactory.

The above model has been tested on some ionic systems over very wide ranges of composition, but over limited ranges of temperature and pressure (42,43). In this study, the model is applied over a wider range of temperature and pressure, from 25-350°C and from 1 bar or saturation pressure to 1 kb. NaCl and KCl are major solute components in natural fluids and there are abundant experimental data from which their parameters can be evaluated. While models based on the ion-interaction approach are available for NaCl(aq) and KCl(aq) (12,16), these are valid only to about 6 molal. Solubilities of NaCl and KCl in water, however, reach 12 and 20 m, respectively, at 350°C, and ionic strengths of NaCl-KCl solutions reach more than 30 m at this temperature (44). Our objective is to describe the thermodynamic properties, particularly the osmotic and activity coefficients, of NaCl(aq) and KCl(aq) to saturation concentration in binary salt-H₂O mixtures and in ternary NaCl-KCl-H₂O systems, and to apply the Margules-expansion model to solubility calculations to 350°C.

For purposes of developing general equations for the thermodynamic properties of electrolyte solutions, it is useful to recalculate experimental values to a single reference pressure. This allows experimental data on different solution properties, including activities, enthalpies, and heat capacities, whose relationships with each other are defined on an isobaric basis, to be considered in the overall regression of the model equations. This procedure has been useful for NaCl(aq) (16), KCl(aq) (12), and Na₂SO₄(aq) (13). The parameters required to recalculate thermodynamic data from the experimental to the reference pressure can be determined from a regression of volumetric data. For the Margules-expansion model, the pressure dependence of

the excess Gibbs energy, osmotic coefficient and activity coefficient can be derived from volumetric data as shown below.

The total volume, V , of the solution is given by

$$V = n_1 V_1^{\circ} + n_2 \bar{V}_2^{\circ} + (\partial G^{\text{ex}} / \partial P)_T \quad (31)$$

where V_1° is the molal volume of the solvent, and \bar{V}_2° is the partial molal volume of the salt at infinite dilution. The apparent molal volume, ϕ_V , is given by

$$\phi_V = (V - n_1 V_1^{\circ}) / n_2 \quad (32)$$

so that

$$\phi_V = \bar{V}_2^{\circ} + (1/n_2) (\partial G^{\text{ex}} / \partial P)_{T, n_1, n_2} \quad (33)$$

Equations (24) and (25) for the excess Gibbs energy, and Eqn. (33) then yield

$$\phi_V = (A_{V,x} / \rho) \ln(1 + \rho I^{1/2}) + \bar{V}_2^{\circ} - 2RTx_2 [W_{1,MX}^V - x_1 U_{1,MX}^V] \quad (34a)$$

where

$$A_{V,x} = \Omega^{1/2} A_V \quad (34b)$$

$$W_{1,MX}^V = (\partial W_{1,MX} / \partial P)_T \quad (34c)$$

$$U_{1,MX}^V = (\partial U_{1,MX} / \partial P)_T \quad (34d)$$

and A_V is defined in Eqn. (15d).

Equations (34c) and (34d) relate the volumetric parameters $W_{1,MX}^V$ and $U_{1,MX}^V$ to the pressure dependence of the parameters $W_{1,MX}$ and $U_{1,MX}$ for the excess Gibbs energy and osmotic/activity coefficients. In this study we have evaluated $W_{1,MX}^V$ and $U_{1,MX}^V$ for NaCl(aq) at temperatures 25–350°C and pressures from 1 bar or saturation pressure to 1 kb, based on apparent molal volumes calculated from the equations of Rogers and Pitzer (15), plus additional experimental data not considered in their study (45–47). Initial regressions of Eqn. (34) to isothermal and isobaric sets of experimental values indicated the P and T dependence of \bar{V}_2° , $W_{1,MX}^V$ and $U_{1,MX}^V$. Excellent fits are normally obtained to isobaric-isothermal sets of data. Examples are shown in Fig. 5

for apparent molal volumes at 350°C and pressures to 1 kb. The curves are calculated values at the indicated pressures using parameters listed in Table 2.

The next step is to perform a simultaneous regression of NaCl(aq) apparent molal volumes from 25-350°C. Over this wide range of temperature, however, and particularly above 300°C, standard-state properties based on the infinitely dilute reference state exhibit a very complex behavior (15, 16) which is related to the various peculiarities of the solvent. Thus in their representation of NaCl(aq) volumetric properties, Rogers and Pitzer (15) adopted a reference composition of a "hydrated fused salt", NaCl·10H₂O, in order to minimize the P and T dependence of the standard state volume and to be able to adequately fit volumetric data to 300°C and 1 kb. In this study we use the (supercooled) fused salt as the reference state. The equation for the apparent molal volume on this basis can be easily derived from that for the excess Gibbs energy of Pitzer and Simonson (40), and is given by

$$\begin{aligned} \phi V = & (A_{V,X}/\rho) \ln[(1+\rho I_X^{1/2})/(1+\rho(I_X^\circ)^{1/2})] + v_2^{\circ,fs} \\ & + 2RTx_1 (w_{1,MX}^V + x_2 U_{1,MX}^V), \end{aligned} \quad (35)$$

where I_X° represents I_X for a pure fused salt and is 1/2 for salts of singly-charged ions, while $v_2^{\circ,fs}$ is the molal volume for a (supercooled) fused salt. Values for the infinitely dilute reference state can be calculated from $v_2^{\circ,fs}$ using the relation

$$v_2^\circ = v_2^{\circ,fs} + 2RTw_{1,MX}^V - (A_{V,X}/\rho) \ln(1+\rho(I_X^\circ)^{1/2}). \quad (36)$$

Apparent molal volumes of NaCl solutions from 25-350°C were used to fit Eqn. (35) and the following P and T function for $v_2^{\circ,fs}$, $w_{1,MX}^V$, and $U_{1,MX}^V$:

$$f(T,P) = A + BP + CP^2 \quad (37a)$$

where

$$A = q_1 + q_2/T + q_3T + q_4T^2 + q_5/(647-T)^2 \quad (37b)$$

$$B = q_6 + q_7/T + q_8T + q_9T^2 + q_{10}/(647-T)^2 \quad (37c)$$

$$C = q_{11} + q_{12}/T + q_{13}T + q_{14}T^2 + q_{15}/(647-T)^2. \quad (37d)$$

Up to 300°C, the overall regression included values at pressures to 1 kb. At 350°C, however, only volumetric data at pressures less than or equal to 200 bars were included because the simple pressure function given by Eqn. (36a) is inadequate to fit the 350°C data over the whole pressure range. The parameters for Eqn. (37) for $V_2^{\circ,fs}$, $W_{1,MX}^V$, and $U_{1,MX}^V$ evaluated from the volumetric data are given in Table 3. With this set of parameters it is now possible to recalculate various thermodynamic properties of NaCl(aq) solutions to a reference pressure, here chosen to be 200 bars. Because the volumetric data for KCl solutions are more limited in concentration range and are less precise than those for NaCl solutions (12), a separate evaluation of KCl(aq) volumetric data was not done. Instead, the pressure dependence of KCl(aq) properties was approximated using the values for NaCl(aq). This procedure has been successful for Na₂SO₄(aq) (13).

Our principal interests in this study are osmotic and activity coefficients of NaCl(aq) and KCl(aq) solutions at temperatures to 350°C and up to saturation concentration. In the range 25-300°C and at 1 bar or saturation pressure, NaCl(aq) osmotic coefficients up to 4 m were taken from a comprehensive thermodynamic treatment of Pitzer et al. (16). Above 4 m, the values were taken from Liu and Lindsay (48). At temperatures above 300°C, osmotic coefficients were calculated from vapor pressure data of Wood et al. (48). Additional vapor pressure data are given in 50-56, but these are less precise measurements and were given smaller weights in the regression. For KCl(aq), osmotic coefficients to 6 m at temperatures from 25-325°C at 1 bar or saturation pressure were taken from the ion-interaction model of Pabalan and Pitzer (12). Additional values up to 350°C and saturation concentration were

derived from 49, 50, 53, and 57.

Osmotic coefficients of NaCl and KCl solutions from these various sources were recalculated to the reference pressure of 200 bars. An overall regression to each isobaric set of data was done to determine values of $W_{1,MX}$ and $U_{1,MX}$ as functions of temperature using Eqn. (16). The parameters for NaCl(aq) and KCl(aq) evaluated from the osmotic coefficients are given in Table 4. These parameters, together with those of Table 3, permit the calculation of osmotic and activity coefficients of NaCl and KCl solutions to saturation concentration at pressures to 1 kb from 25-350°C, and at pressures to 200 bars above 300°C.

For solubility calculations we need the Gibbs energy values for the solid (58) and for the aqueous species. The latter can be derived from equations for standard state heat capacities given by Pitzer et al. (16) and Pabalan and Pitzer (12) for NaCl(aq) and KCl(aq), respectively, or from the equation of state for standard state properties of electrolytes given by Tanger and Helgeson (59). In our calculations, we have used the former equations to 300°C, and the latter above 300°C. Predicted solubilities for NaCl and KCl in water to 350°C are compared with experimental values from various sources in Figs. 6 and 7, respectively. The agreement is very good, although there are substantial differences between various measurements for KCl.

Of more interest are solubility calculations in the ternary system NaCl-KCl-H₂O. The equations for the excess Gibbs energy and activity coefficients in a mixture of a solvent and two salts with a common ion, MX and NX, and with cation fraction F of M are given by Pitzer and Simonson (40). Their equation for the activity coefficient of the solute MX in the ternary mixture MX-NX-H₂O based on a pure fused salt standard state can be converted to one based on the infinitely dilute reference state. This is given by

$$\ln(\gamma_M^* \gamma_X^*) = -2A_X \left\{ \frac{2}{\rho} \ln(1 + \rho I_X^{1/2}) + I_X^{1/2} \frac{(1 - 2I_X)}{(1 + \rho I_X^{1/2})} \right\} \quad (38)$$

$$+ 2[x_I(1 - x_I F) - 1]W_{1, MX} + 2x_I x_I \{(1 - F + 2Fx_I)U_{1, MX}$$

$$- (1 - F)[W_{1, NX} + (x_I - x_I)U_{1, NX}]\} + x_I(1 - F)\{(1 - x_I F)W_{MX, NX}$$

$$+ x_I[3F - 1 + 2x_I F(1 - 2F)U_{M, N}]\} + 2x_I(1 - 2x_I F)Q_{1, MX, NX},$$

where the total mole fraction of ions $x_I = (1 - x_I)$, whereupon $x_M = Fx_I/2$, $x_N = (1 - F)x_I/2$, and $x_X = x_I/2$. The corresponding equation for $(\gamma_N^* \gamma_X^*)$ can be obtained from Eqn. (38) by interchanging subscripts and replacing F with $(1 - F)$. It should be noted that for the general case of a ternary system $MX-NX-H_2O$, all but one of the parameters, namely $Q_{1, MX, NX}$, can be determined from the binary systems. In the particular case of $NaCl-KCl-H_2O$, however, the temperatures of interest are below the melting point of $NaCl$ and KCl . Thus $W_{NaCl, KCl}$ and $U_{Na, K}$, together with $Q_{1, NaCl, KCl}$ have to be evaluated from activity data in the ternary system. Values of $W_{1, NaCl}$, $W_{1, KCl}$, $U_{1, NaCl}$, and $U_{1, KCl}$ have been previously determined from binary $NaCl$ and KCl solutions.

Robinson (60) provides precise isopiestic data for the $NaCl-KCl-H_2O$ at $25^\circ C$, while Holmes and Mesmer (61) provide data at 110, 140, 172, and $201^\circ C$. These measurements, however, extend only to ionic strengths of about 7.5 m, whereas the maximum solubility in the system already exceeds this value at $50^\circ C$, and reaches more than 30 m at $350^\circ C$. It is apparent that values of $W_{NaCl, KCl}$, $U_{Na, K}$, and $Q_{1, NaCl, KCl}$ could be best determined from solubility data in mixtures of $NaCl$ and KCl solutions. These are available from the tabulation of Linke (25) and the extensive evaluation of Sterner et al.

(44). It was found sufficient to assume a zero value for $U_{Na, K}$, a constant $Q_{1, NaCl, KCl}$ equal to 0.9547, and a temperature dependent equation for $W_{NaCl, KCl}$ given by Eqn. (16) for which q_1 , q_2 , q_3 , q_4 and q_5 have values of $1.778998E+03$, $-3.19436E+02$, $-4.64165E+04$, $7.33463E-01$, and $-2.80959E-04$, respectively, and zero for q_6 and q_7 . Solubilities calculated from these

parameters and those given in Tables 3 and 4 are compared to experimental data in Fig. 8. Our calculated values agree very well with those of Sterner et al. (44), mostly within 2% and not exceeding 5%. Standard deviations between osmotic coefficients calculated using these parameters and experimentally determined values are 0.004, 0.004, 0.005, 0.007, and 0.008 for temperatures of 25, 110, 140, 172, and 201°C, respectively.

ACKNOWLEDGEMENT

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Table 1. Equations for the osmotic coefficient, activity coefficient, apparent molal enthalpy, heat capacity and volume of a binary electrolyte solution based on the ion-interaction model.^a

Osmotic coefficient

$$(10a) \quad \phi - 1 = -|z_M z_X| A_\phi I^{1/2} / (1 + bI^{1/2}) + (2\nu_M \nu_X / \nu) [mB_{MX}^\phi + m^2 (\nu_M \nu_X)^{1/2} C_{MX}^\phi]$$

$$(10b) \quad B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \exp(-\alpha_2 I^{1/2})$$

$$(10c) \quad C_{MX}^\phi = C_{MX}^\phi / 2 |z_M z_X|^{1/2}$$

Activity Coefficient

$$(11a) \quad \ln \gamma_\pm = -|z_M z_X| A_\phi [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] \\ + (2\nu_M \nu_X / \nu) [mB_{MX}^Y + m^2 (\nu_M \nu_X)^{1/2} C_{MX}^Y]$$

$$(11b) \quad B_{MX}^Y = 2\beta_{MX}^{(0)} + \beta_{MX}^{(1)} [g(\alpha_1 I^{1/2}) + \exp(-\alpha_1 I^{1/2})] \\ + \beta_{MX}^{(2)} [g(\alpha_2 I^{1/2}) + \exp(-\alpha_2 I^{1/2})]$$

$$(11c) \quad C_{MX}^Y = 3C_{MX}^\phi / 2$$

$$(11d) \quad g(x) = 2[1 - (1+x)\exp(-x)] / x^2$$

Apparent Molal Enthalpy

$$(12a) \quad \phi^L = \nu |z_M z_X| A_H \ln(1 + bI^{1/2}) / 2b - 2\nu_M \nu_X RT^2 [mB_{MX}^L + m^2 (\nu_M \nu_X) C_{MX}^L]$$

$$(12b) \quad B_{MX}^L = (\partial B_{MX} / \partial T)_{P, I} \\ = \beta_{MX}^{(0)L} + \beta_{MX}^{(1)L} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)L} g(\alpha_2 I^{1/2})$$

$$(12c) \quad \beta_{MX}^{(i)L} = (\partial \beta_{MX}^{(i)} / \partial T)_{P, I} \quad i = 0, 1, 2$$

$$(12d) \quad C_{MX}^L = (\partial C_{MX} / \partial T)_{P, I} = (\partial C_{MX}^\phi / \partial T)_{P, I} / 2 |z_M z_X|^{1/2}$$

Apparent Molal Heat Capacity

$$(13a) \quad \phi^J = \bar{C}_p^\circ + \nu |z_M z_X| A_J \ln(1 + bI^{1/2}) / 2b - 2\nu_M \nu_X RT^2 [mB_{MX}^J + m^2 (\nu_M \nu_X) C_{MX}^J]$$

$$(13b) \quad B_{MX}^J = (\partial^2 B_{MX} / \partial T^2)_{P, I} + (2/T) (\partial B_{MX} / \partial T)_{P, I}$$

$$= \beta_{MX}^{(0)J} + \beta_{MX}^{(1)J} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)J} g(\alpha_2 I^{1/2})$$

$$(13c) \quad \beta_{MX}^{(i)J} = (\partial^2 \beta_{MX}^{(i)} / \partial T^2)_P + (2/T) (\partial \beta_{MX}^{(i)} / \partial T)_P, \quad i = 0, 1, 2$$

$$(13d) \quad C_{MX}^J = (\partial^2 C_{MX} / \partial T^2)_P + (2/T) (\partial C_{MX} / \partial T)_P$$

Apparent Molal Volume

$$(14a) \quad \phi_V = \bar{V}_2^\circ + \nu |z_M z_X| A_V \ln(1 + bI^{1/2}) / 2b + 2\nu_M \nu_X RT [m B_{MX}^V + m^2 (\nu_M z_M) C_{MX}^V]$$

$$(14b) \quad B_{MX}^V = (\partial B_{MX} / \partial P)_{T,I}$$

$$= \beta_{MX}^{(0)V} + \beta_{MX}^{(1)V} g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)V} g(\alpha_2 I^{1/2})$$

$$(14c) \quad \beta_{MX}^{(i)V} = (\partial \beta_{MX}^{(i)} / \partial P)_T, \quad i = 0, 1, 2$$

$$(14d) \quad C_{MX}^V = (\partial C_{MX} / \partial P)_T = (\partial C_{MX}^\phi / \partial P)_T / 2 |z_M z_X|^{1/2}$$

Debye-Hückel Slopes

$$(15a) \quad A_\phi = 1/3 (2\pi N_0 d_w / 1000)^{1/2} [e^2 (DkT)]^{3/2}$$

$$(15b) \quad A_H = 4RT^2 (\partial A_\phi / \partial T)_P$$

$$(15c) \quad A_J = (\partial A_H / \partial T)_P$$

$$(15d) \quad A_V = -4RT (\partial A_\phi / \partial P)_T$$

^aDefinition of symbols: b = a general constant with value $1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$; the β 's and C^ϕ are ion-interaction parameters specific to each solute MX; $\beta_{MX}^{(2)}$ is zero unless both ions have charge 2 or greater; $\alpha_1 = 2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ unless both ions have charge 2 or greater whereupon $\alpha_1 = 1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ and $\alpha_2 = 12 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$; I = ionic strength ($1/2 \sum m_i z_i^2$); ν = total number of ions formed from the salt ($\nu = \nu_M + \nu_X$); z_M and z_X are the charges on the ions; $\bar{C}_{p,2}^\circ$ = apparent or partial molal heat capacity of the solute at infinite dilution; \bar{V}_2° = apparent or partial molal volume of the solute at infinite dilution; D = dielectric constant of water; d_w = density of pure water; e = electronic charge; k = Boltzmann constant.

Table 2. Parameters for Eqn. (34) evaluated from isothermal-isobaric apparent molal volumes of NaCl solutions at 350°C and various pressures.

P(bars)	\bar{V}_2^0	$W_{1,MX}^V$	$U_{1,MX}^V$
Psat	-4.46598E+02	3.14714E-03	2.62327E-03
200.	-3.86510E+02	2.15334E-03	1.29351E-03
300.	-2.29832E+02	1.57804E-04	-9.31161E-04
400.	-1.57793E+02	-1.14738E-04	-5.35688E-04
500.	-1.15825E+02	-4.49861E-04	-5.68718E-04
600.	-8.92339E+01	-5.79236E-04	-5.00818E-04
800.	-5.90148E+01	-2.77794E-04	1.79049E-04
1000.	-4.07166E+01	-2.54388E-04	2.81882E-04

Table 3. Parameters for Eqns. (35) and (37) evaluated from apparent molal volumes of NaCl solutions up to 350°C and 1 kb.

	v_2^0, fs	$w_{1, MX}^V$	$U_{1, MX}^V$
q ₁	-6.434497E+02	-1.724835E-02	-2.9789818E-02
q ₂	0.0	3.347333E+00	5.7872110E+00
q ₃	3.554544E+00	1.996689E-05	3.5321836E-05
q ₄	-4.612823E-03	3.861388E-09	6.7591836E-09
q ₅	-3.254781E+05	4.273295E+00	4.4639601E+00
q ₆	4.496614E-01	3.318704E-06	1.2359971E-05
q ₇	-2.830405E+01	-6.183551E-04	-2.0125079E-03
q ₈	-2.047906E-03	0.0	-1.7757055E-08
q ₉	2.627796E-06	-9.914615E-12	0.0
q ₁₀	1.948423E+03	-2.048634E-02	-2.9326904E-02
q ₁₁	-1.201087E-04	0.0	0.0
q ₁₂	1.327249E-02	0.0	0.0
q ₁₃	3.539774E-07	0.0	0.0
q ₁₄	-3.546851E-10	0.0	0.0
q ₁₅	1.263778E-01	0.0	0.0

Table 4. Parameters for Eqn. (16) for $W_{1,MX}$ and $U_{1,MX}$ for NaCl and KCl solutions evaluated from osmotic coefficients up to 350°C at a reference pressure of 200 bars.

	$W_{1,NaCl}$	$U_{1,NaCl}$	$W_{1,KCl}$	$U_{1,KCl}$
q_1	1.0620140E+03	2.2783431E+03	1.870602E+03	3.999606E+03
q_2	-2.3263776E+04	-5.5141510E+04	-5.071750E+04	-1.063245E+05
q_3	-2.0149086E+02	-4.2036595E+02	-3.326169E+02	-7.145462E+02
q_4	6.1763652E-01	1.1574638E+00	7.159419E-01	1.610570E+00
q_5	-2.9491559E-04	-5.3640257E-04	-2.458959E-04	-6.069845E-04
q_6	0.0	0.0	0.0	0.0
q_7	0.0	2.5441911E+01	-1.634611E+01	0.0

FIGURE CAPTIONS

- Fig. 1. Solubilities of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4) in water as a function of temperature. The symbols are experimental data tabulated by Linke (25), and the curves are predicted values.
- Fig. 2. Calculated solubilities in the $\text{NaCl-Na}_2\text{SO}_4\text{-H}_2\text{O}$ system compared with experimental data from Linke (25) to 100°C and from Schroeder et al. (26) at 150°C and above. The intersections of isothermal curves represent calculated triple points.
- Fig. 3. Calculated solubilities in the $\text{Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$ system compared with experimental data from Linke (25) to 100°C and from Schroeder et al. (26) above 100°C .
- Fig. 4. Calculated and experimental solubilities of thenardite (Na_2SO_4) at fixed molalities of NaOH in the quaternary system $\text{NaCl-Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$ at: a) 200°C , and b) 300°C . The symbols are experimental data from Schroeder et al. (26).
- Fig. 5. Apparent molal volumes of NaCl(aq) solutions at 350°C and pressures to 1 kb. The curves are calculated from Eqn. (34) and the parameters given in Table 2.
- Fig. 6. Solubilities of halite (NaCl) in water to 350°C . The curve represents values calculated using the Margules-expansion model for activity coefficients (infinite dilution reference state), and standard state Gibbs energies for NaCl(aq) derived from the equations of Pitzer et al. (16) to 300°C , and of Tanger and Helgeson (59) above 300°C .
- Fig. 7. Solubilities of sylvite (KCl) in water to 350°C . The curve represents values calculated using the Margules-expansion model for activity coefficients (infinite dilution reference state), and standard state Gibbs energies for KCl(aq) derived from the equations of Pabalan and Pitzer (12) to 300°C , and of Tanger and Helgeson (59) above 300°C .
- Fig. 8. Solubilities of halite and/or sylvite in the $\text{NaCl-KCl-H}_2\text{O}$ system. The squares and circles are experimental data taken from Sterner et al. (44) and Linke (25), respectively (open symbols for halite, closed symbols for sylvite). The open triangles are triple point (halite+sylvite+saturated solution) data from Linke, and the closed triangles are triple point data from Sterner et al. The curves are calculated as in Figs. 6 and 7.

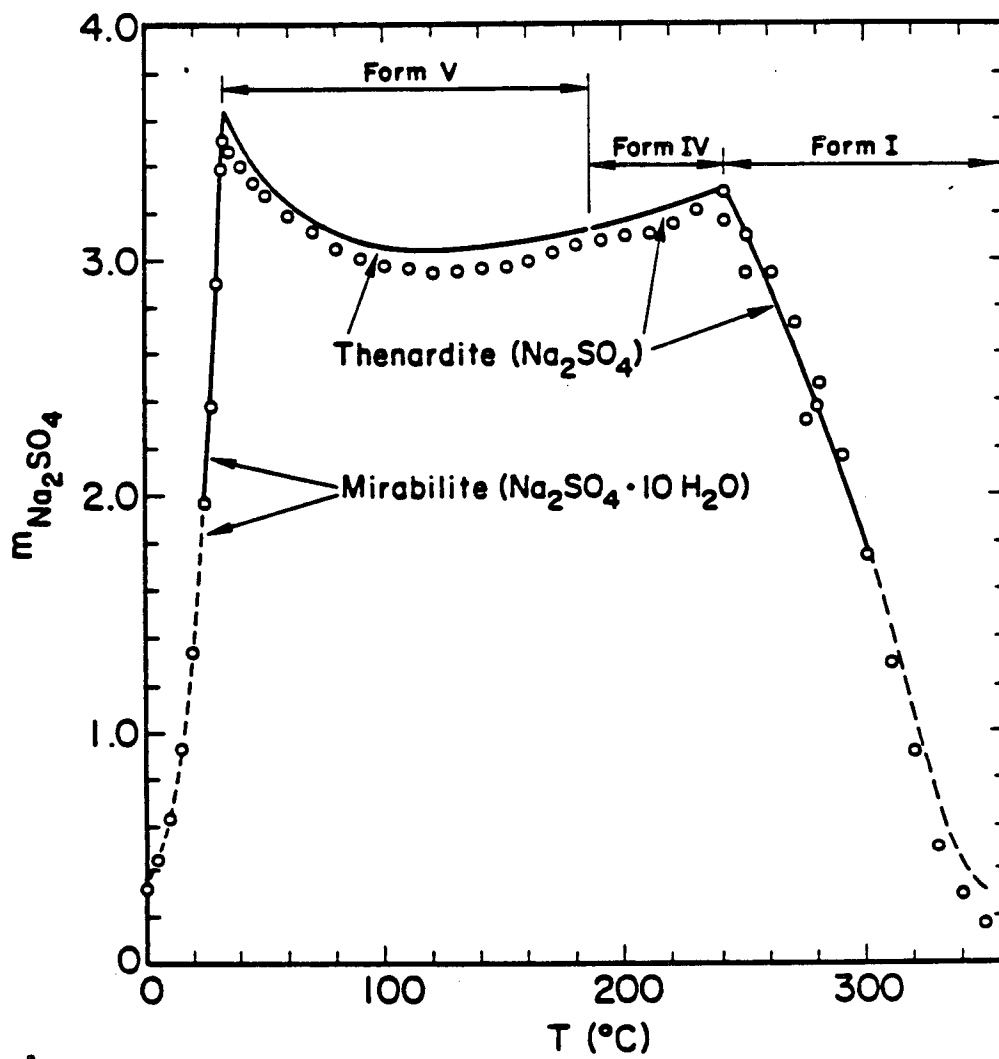


Figure 1.

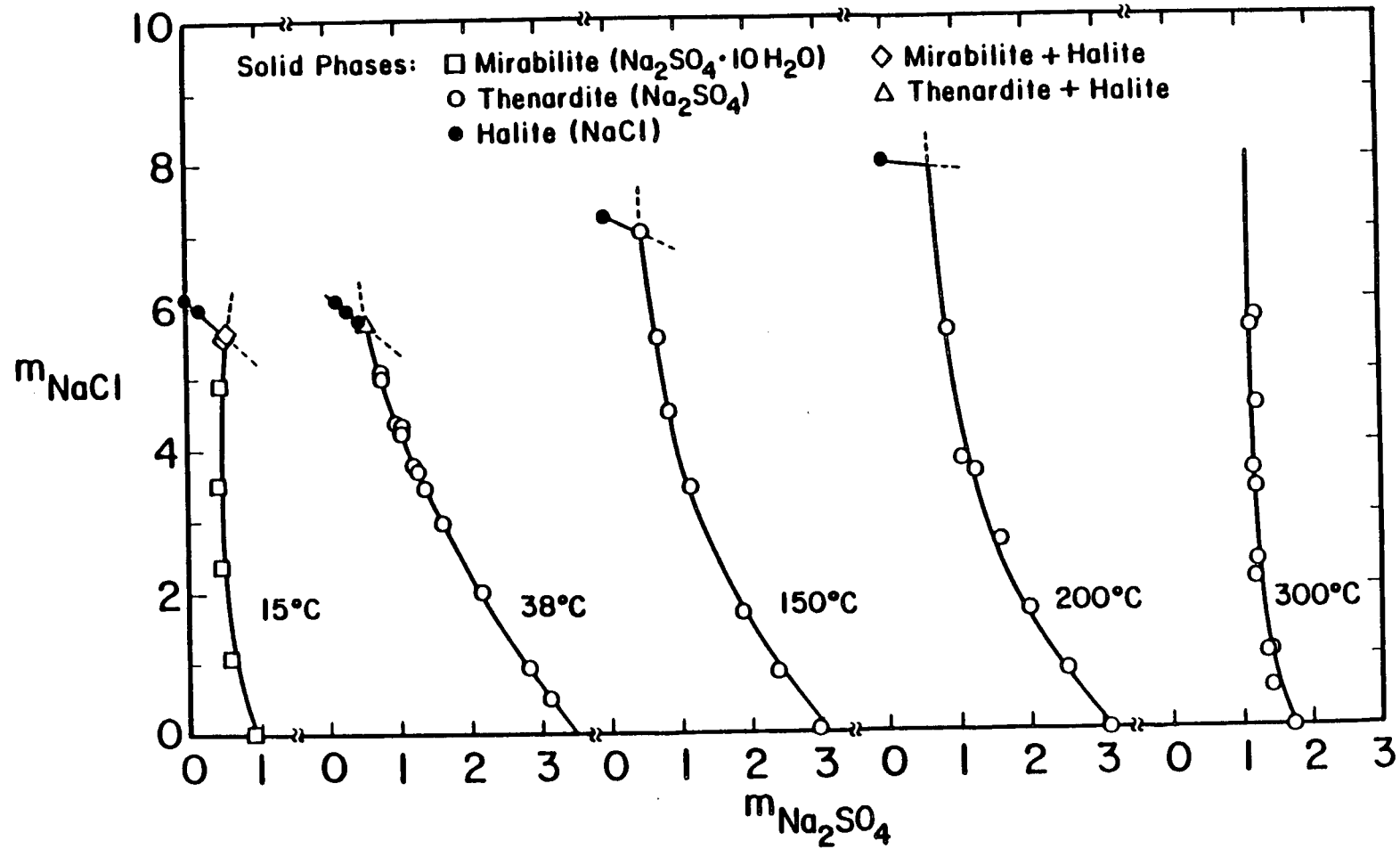


Figure 2.

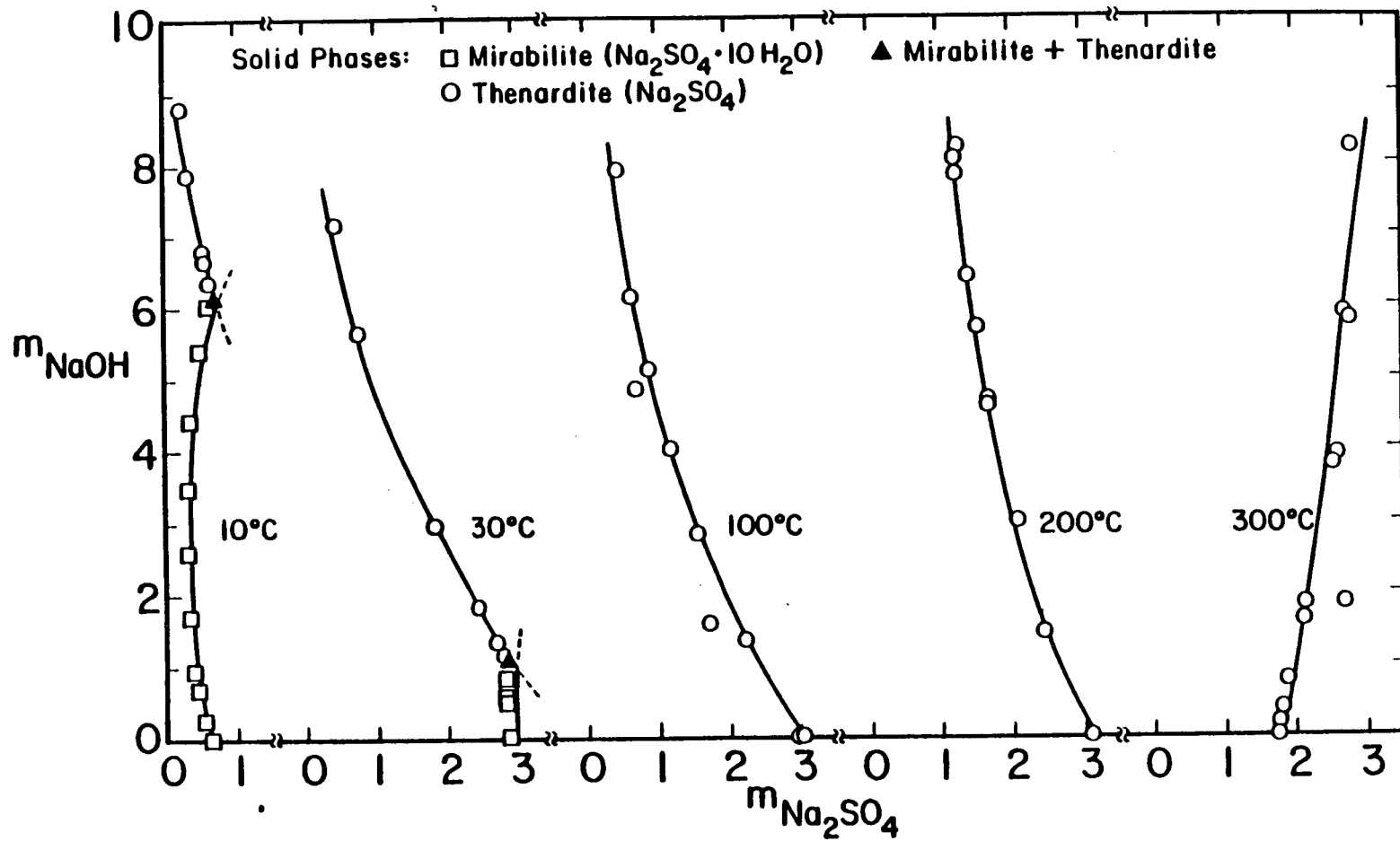


Figure 3.

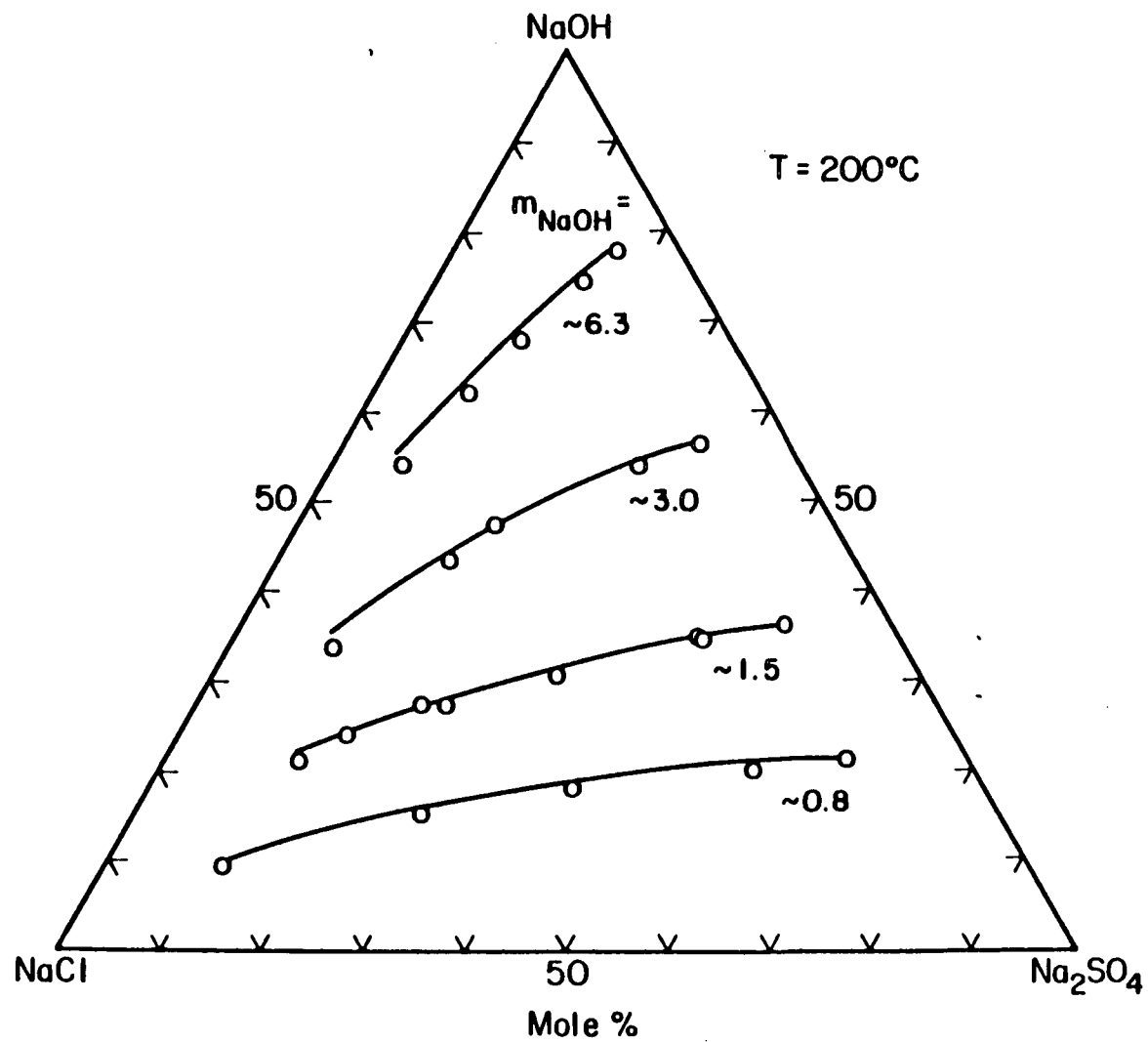


Figure 4a.

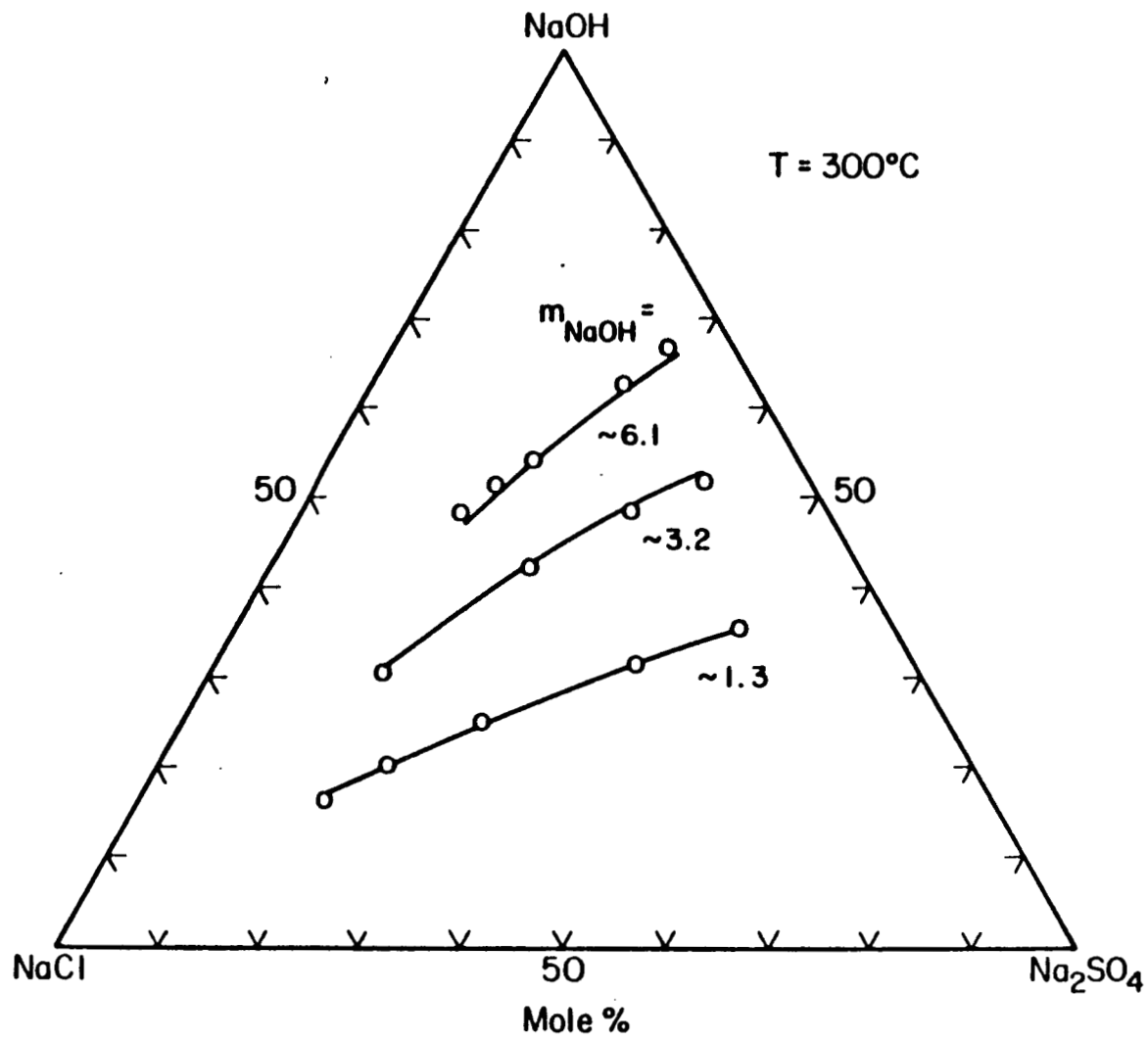


Figure 4b.

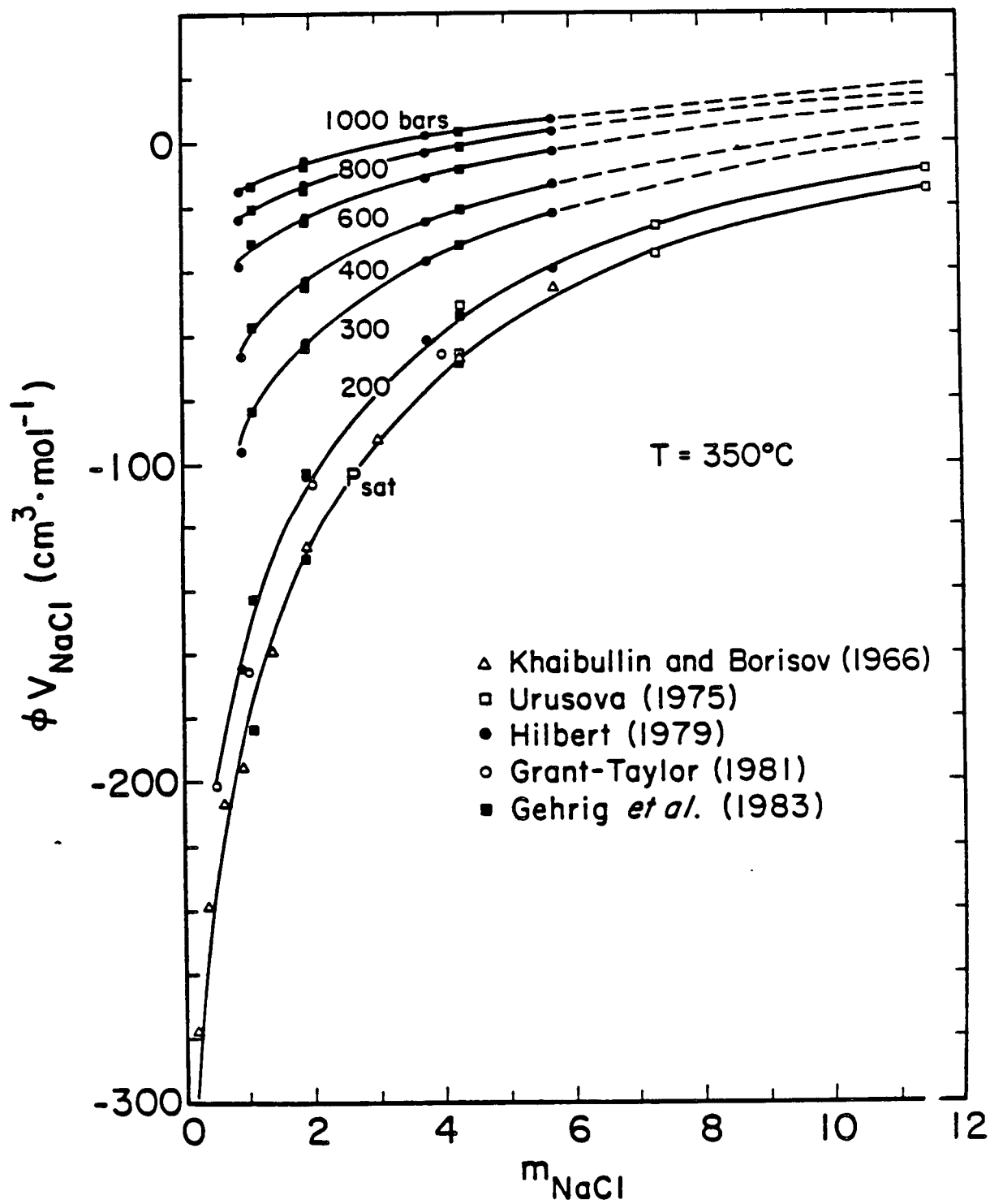


Figure 5.

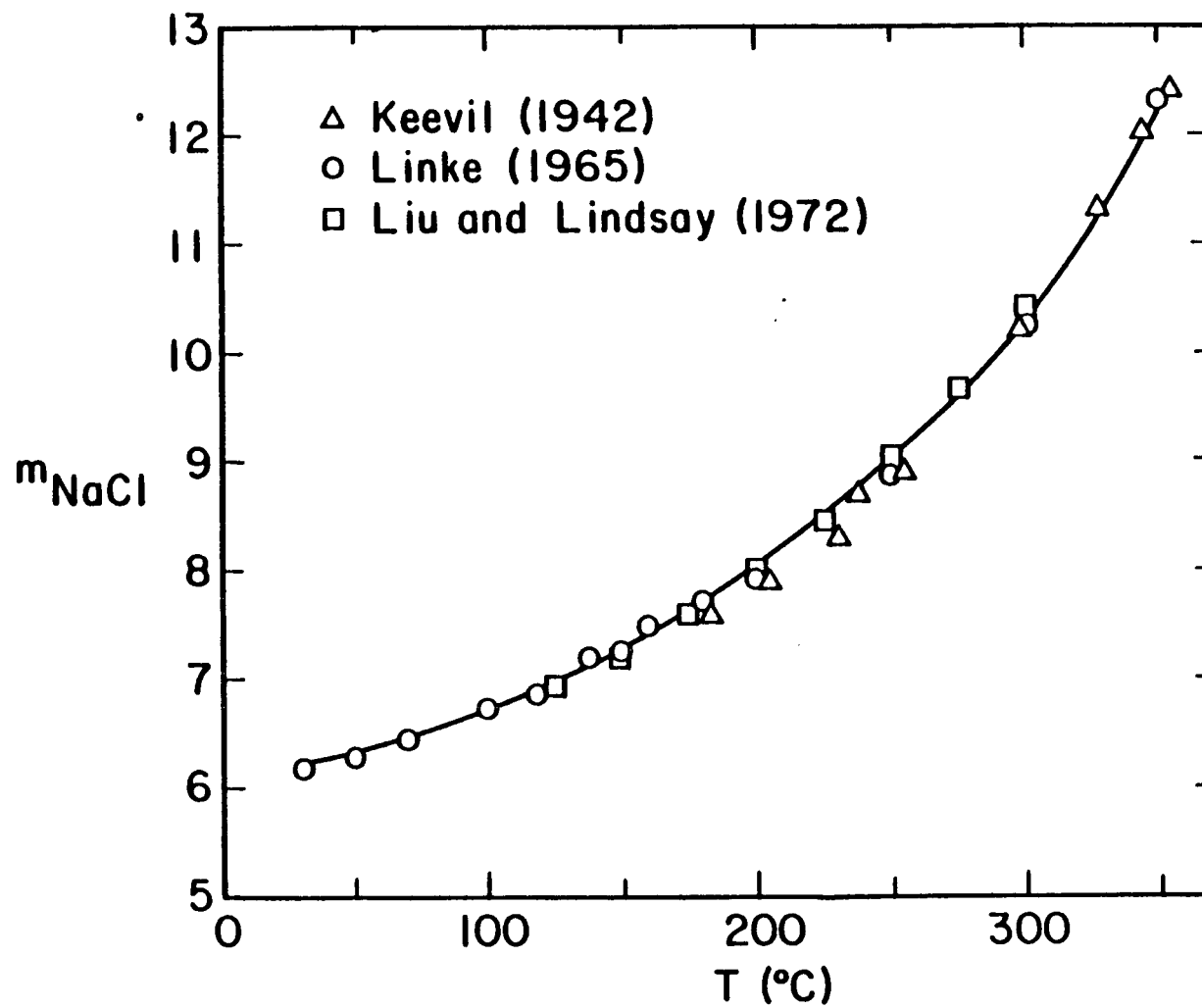


Figure 6.

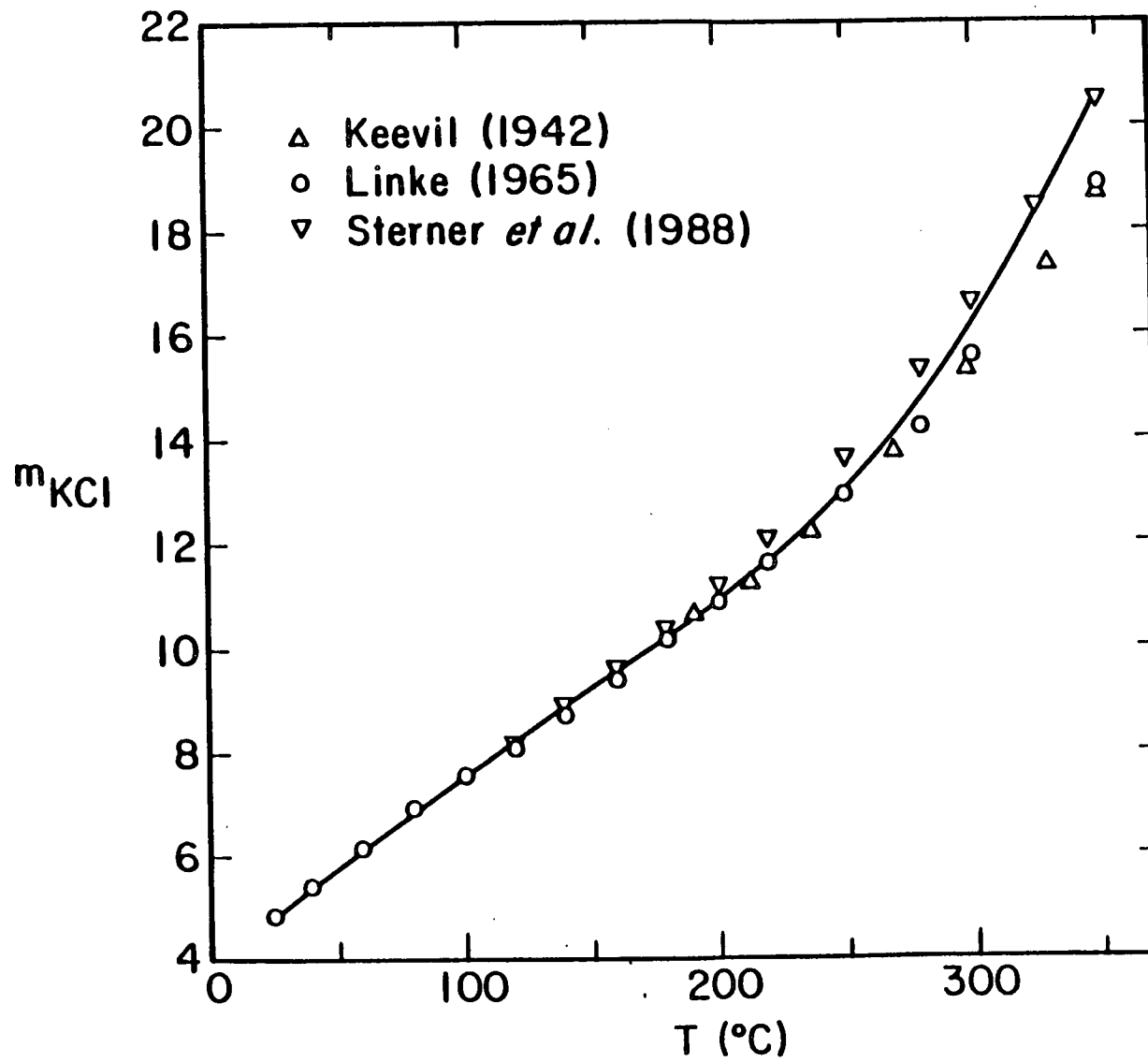


Figure 7.

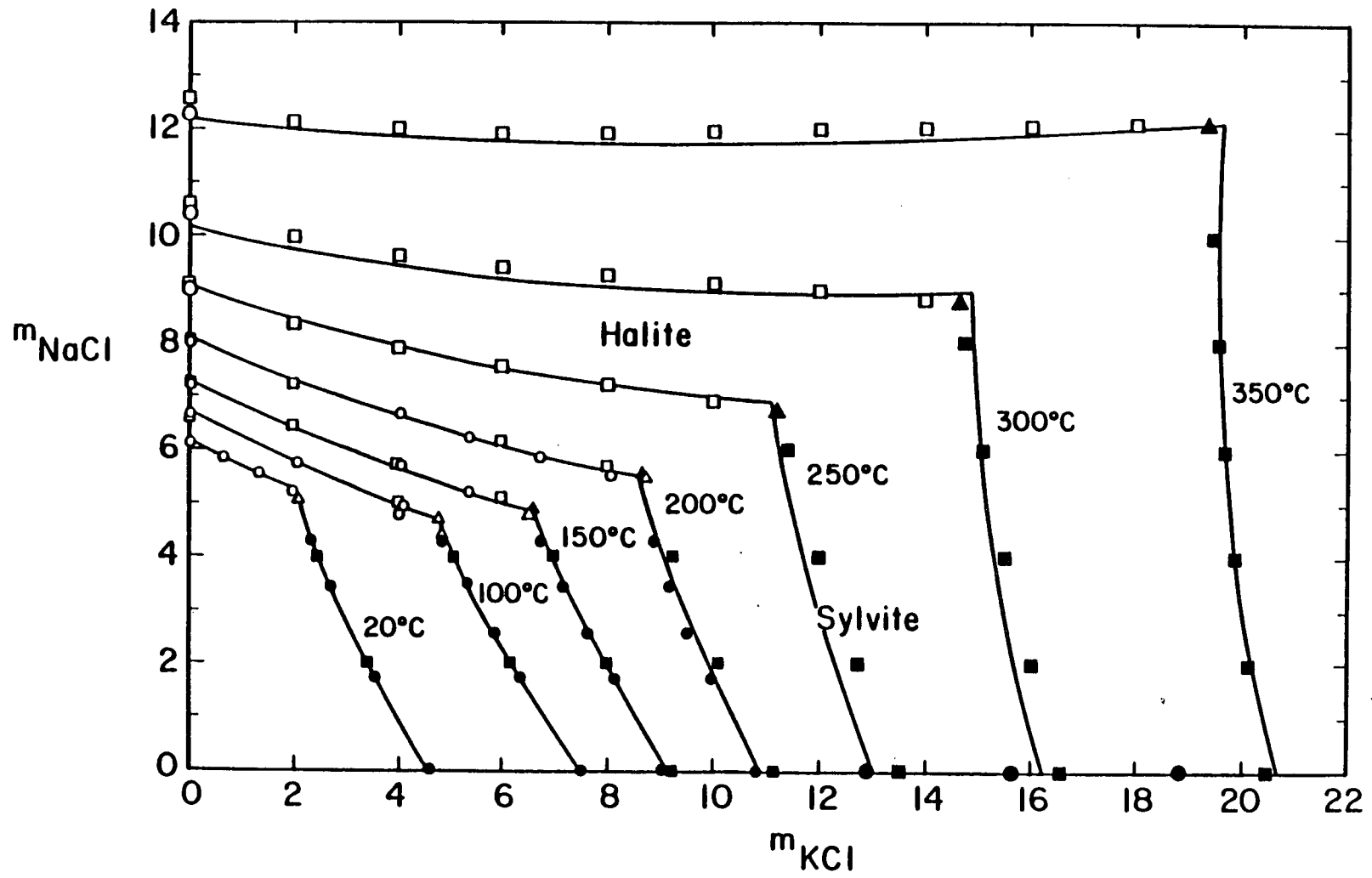


Figure 8.