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Authors

Pitzer, Kenneth S.
Sternner, S.M.

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**Equations of State for Solid NaCl-KCl
and Liquid NaCl-KCl-H₂O**

K. S. Pitzer and S. M. Sterner

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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EQUATIONS OF STATE FOR SOLID NaCl-KCl AND LIQUID NaCl-KCl-H₂O

Kenneth S. Pitzer and S. Michael Sterner

Department of Chemistry, University of California
and
Chemical Sciences Division, Lawrence Berkeley Laboratory
1 Cyclotron Road, Berkeley, CA 94720 (U.S.A.)

ABSTRACT

The equilibrium between the solid solution of NaCl-KCl and the ternary liquid NaCl-KCl-H₂O is both scientifically interesting and geologically important. Equations of the Margules type have been derived for the two phases that accurately reproduce the extensive array of published measurements, together with recent measurements of Chou for the liquidus of the ternary and the solidus of the NaCl-KCl binary. The range of validity of the equations extends to 1200 K, to 5 kbar, but for aqueous systems it is limited to compositions on the salt saturation surface. Of particular interest is the transition in the liquid-solid equilibrium of the ternary from the pattern at high temperatures where the solid is a solution of composition near that of the liquid to that at lower temperatures where the solid is nearly pure NaCl or KCl. The phase compositions for anhydrous NaCl-KCl are consistent with the heat of mixing data of Hersh and Kleppa and yield a new expression for the entropy of mixing.

1. INTRODUCTION

The ternary liquid system NaCl-KCl-H₂O is of considerable interest in geological and other practical situations, as well as being important as a prototype of a ternary aqueous liquid in equilibrium with either one or two solid solutions.

The halite and sylvite liquidus in the NaCl-H₂O, KCl-H₂O, and NaCl-KCl binary systems and within the NaCl-KCl-H₂O ternary system and the solidus in the NaCl-KCl binary system have been measured by Chou (1982), Gunter et al. (1983), Chou (1987), and Chou et al. (1991). In addition, Chou et al. (1991) review published experimental determinations of the solvus gap in the NaCl-KCl anhydrous binary as well as the general topology of the solid-liquid phase relations in the full ternary system. Here we present a thermodynamic model for the NaCl-KCl solid and the NaCl-KCl-H₂O ternary liquid that satisfies the observed phase equilibrium behavior. It agrees also with the heat of mixing of liquid NaCl-KCl (Hersh and Kleppa, 1965).

The total Gibbs free energy in the NaCl-KCl-H₂O system was expressed using two independent equations of state -- one for the solid and one for the liquid phase. Each equation has terms representing the ideal Gibbs energy of mixing and a Margules expression for the excess Gibbs energy. The Margules expression for the solids in the NaCl-KCl-H₂O system is a function only of the

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NaCl and KCl components since no solid solution exists between H₂O and NaCl-KCl. For the liquid phase, a separate Margules expression was formulated for each binary subsystem. The equation for the NaCl-KCl binary should be valid over the entire composition range but the equations for the aqueous binaries are valid only for solid-saturated compositions. The model for the excess Gibbs energy of the ternary liquid was obtained by combining the individual binary expressions together with one additional term to account for three-particle interactions between ternary components. This equation is likewise valid for all anhydrous liquid compositions but only solid-saturated aqueous compositions. The form and complexity chosen for each excess Gibbs energy model represents a balance between goodness of fit to the experimental data and an attempt to avoid overfitting.

Since no information was introduced for the chemical potential of water and there was only one value of the salt chemical potential at any P and T, there is no constraint on the Margules function for an aqueous liquid at compositions other than those of solid saturation. It is well known that the behavior of these aqueous binaries is much more complex than could be described by a single Margules term together with ideal entropy of mixing. At pressures between that of the three-phase assemblage and that of the critical line there is vapor-liquid phase separation. Also, at extreme dilution at any pressure there is salt dissociation into ions which is not considered in our entropy of mixing term. Other equations have been presented for these salt-water systems, in particular, for P-T-X ranges above 350°C (Pitzer and Li, 1983; Tanger and Pitzer, 1989; Hovey et al., 1990), while Pabalan and Pitzer (1990) review treatments below 300°C and present an extension to 350°C. To attempt a more comprehensive treatment of the aqueous systems over their full composition ranges would unduly complicate the present treatment at best and probably detract substantially from the accuracy for the properties here treated. For the anhydrous liquid or solid, however, the data covers the full mole-fraction range and there is no composition limitation on the validity of the equations.

Three types of NaCl-KCl binary PTX data were simultaneously fitted. In addition, the heat of mixing of liquid NaCl-KCl was constrained to the value of Hersh and Kleppa (1965). At high temperatures, crystalline NaCl-KCl solid solutions of given compositions coexist in equilibrium with molten NaCl-KCl liquids generally of different compositions. Only at the minimum melting point are the solidus and liquidus compositions identical. The requirement for chemical equilibrium in this high-temperature region is that the chemical potentials of both the NaCl and KCl components in the solid be equal to those in the liquid phase (i.e., $\mu_{i,P,T}^{\text{NaCl}} = \mu_{s,P,T}^{\text{NaCl}}$, and $\mu_{i,P,T}^{\text{KCl}} = \mu_{s,P,T}^{\text{KCl}}$). At somewhat lower temperatures, well below that of minimum melting, a solvus gap appears and two solid phases of different compositions coexist in equilibrium. In this region, chemical equilibrium requires that the chemical potentials of both the NaCl and KCl components in each solid solution phase be the same (i.e., $\mu_{ss_1,P,T}^{\text{NaCl}} = \mu_{ss_2,P,T}^{\text{NaCl}}$, and $\mu_{ss_1,P,T}^{\text{KCl}} = \mu_{ss_2,P,T}^{\text{KCl}}$). In general, evaluation of the coefficients of the Margules expansion requires the compositions of both phases (solid + liquid, or solid + solid) coexisting at each P and T. Owing to limitations in the experimental procedures, this information is rarely available; in the NaCl-KCl system at high temperatures (see Chou et al., 1991) either the liquidus or solidus composition is

known but not both simultaneously for any particular pressure and temperature. However, the fitting procedure we used allowed us to consider individual data points along the liquidus, solidus or on the solvus independently, and thus it was possible to evaluate the coefficients of the Margules expansion for the excess Gibbs energy of mixing for both the solid and liquid phases in this binary without the benefit of coexisting compositions.

Only liquidus data were available within the NaCl-KCl-H₂O ternary. The requirements for chemical equilibrium within this system are virtually the same as those for the NaCl-KCl binary except that the liquid phase contains water, and thus the Margules expansion for the liquid is somewhat more complex.

Further details of the fitting procedure will be given in a later section. We now outline the thermodynamic quantities and relationships used in the development of our equations of state for NaCl-KCl-H₂O liquids and solids.

2. PROPERTIES OF PURE SOLID AND LIQUID SALTS

Since the chemical potentials of NaCl and KCl are the criteria of equilibrium, the difference of chemical potential for fusion is needed for each salt. The pertinent basic properties and their sources are:

$$\text{NaCl: } T_{m,1\text{bar}} = 1074 \text{ K (Robie et al., 1979)}$$

$$\Delta H_{m,1\text{bar},T_m} = 28.158 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Robie et al., 1979)}$$

$$\left(\frac{dP}{dT}\right)_{s/l} = 41.218 \text{ bar}\cdot\text{K}^{-1} \text{ (Chou, 1982)}$$

$$\Delta C_{p,m} = 26.857 - 2.1197 \times 10^{-2} T \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1} \text{ (Robie et al., 1979)}$$

$$\text{KCl: } T_{m,1\text{bar}} = 1043 \text{ K (Robie et al., 1979)}$$

$$\Delta H_{1\text{bar},T_m} = 26.284 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Robie et al., 1979)}$$

$$\left(\frac{dP}{dT}\right)_{s/l} = 39.347 \text{ bar}\cdot\text{K}^{-1} \text{ (Chou, 1982)}$$

$$\Delta C_p = 98.113 - 4.8522 \times 10^{-2} T - 1.3710 \times 10^3 / T^{1/2}$$

$$+ 1.6054 \times 10^6 / T^2 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$$

(Robie et al., 1979; Chase et al., 1985)

These quantities were combined according to standard thermodynamic equations to yield expressions for the change of chemical potential on fusion as a function of temperature and pressure.

$$\Delta\mu_{m,P,T}^{*,NaCl} = 11.539 - 2.6857 \times 10^{-2}T \log T + 1.05985 \times 10^{-5}T^2 \\ + 1.65312 \times 10^{-1}T + 6.3608 \times 10^{-4}(P-1) \quad (1)$$

$$\Delta\mu_{m,P,T}^{*,KCl} = 40.438 - 9.8113 \times 10^{-2}T \log T + 2.4261 \times 10^{-5}T^2 - 5.484T^{1/2} \\ - 8.027 \times 10^2/T + 7.88341 \times 10^{-1}T + 6.4047 \times 10^{-4}(P-1) \quad (2)$$

The units for $\Delta\mu$ are $\text{kJ}\cdot\text{mol}^{-1}$ with P in bars and T in K.

3. THE NaCl-KCl ANHYDROUS BINARY

The NaCl-KCl anhydrous binary system exhibits both solid solution and liquid miscibility. Thus, the chemical potential of each component in either the crystal or liquid is composition-dependent as well as a function of pressure and temperature.

NaCl-KCl Solids

The molar Gibbs energy of the solid phases in the NaCl-KCl binary can be expressed as:

$$G_{s,NaCl-KCl} = X_{NaCl} \mu_{s,P,T}^{*,NaCl} + X_{KCl} \mu_{s,P,T}^{*,KCl} + RTX_{NaCl} \ln X_{NaCl} + RTX_{KCl} \ln X_{KCl} \\ + RTX_{NaCl}X_{KCl} (wa_{NaCl-KCl}^s + wb_{NaCl-KCl}^s X_{NaCl}) \quad (3)$$

where $wa_{NaCl-KCl}^s$ and $wb_{NaCl-KCl}^s$ are both pressure and temperature dependent. The last line of the above expression is a two-coefficient, unsymmetrical Margules expansion in composition that we have chosen to represent the excess Gibbs energy.

The chemical potentials of the NaCl and KCl components in the solid phases within the NaCl-KCl binary are given by the appropriate derivatives of the total Gibbs energy $G = g\sum n_i$.

$$\mu_{ss,P,T}^{NaCl} = \mu_{s,P,T}^{*,NaCl} + RT \ln X_{NaCl} + RT \ln \gamma_{NaCl}^s \quad (4)$$

$$\mu_{ss,P,T}^{KCl} = \mu_{s,P,T}^{*,KCl} + RT \ln X_{KCl} + RT \ln \gamma_{KCl}^s \quad (5)$$

with the activity coefficients expressed as:

$$\ln \gamma_{NaCl}^s = X_{KCl}^2 (wa_{NaCl-KCl}^s + 2wb_{NaCl-KCl}^s X_{NaCl}) \quad (6)$$

$$\ln \gamma_{KCl}^s = X_{NaCl}^2 (wa_{NaCl-KCl}^s + wb_{NaCl-KCl}^s (1 - 2X_{KCl})) \quad (7)$$

The equilibrium compositions for the binary solid solution were taken from the measurements of Barrett and Wallace (1954), Bhardwaj and Roy (1971), and Vestin and Zakovryashin (1979). Regressions of these data with multiterm expressions for the temperature and pressure dependence of wa^s and wb^s indicated which

terms were needed and their approximate values. The final values, however, come from a general regression including the NaCl-KCl liquid binary and the NaCl-KCl-H₂O ternary as described below. The final expressions are:

$$w a_{\text{NaCl-KCl}}^s = \frac{397.88}{T} + 9.2670 - 0.017728T + (8.8543E-6)T^2 \\ + (P-1) \left(-1.1724E-4 + \frac{0.14768}{T} \right) \quad (8)$$

$$w b_{\text{NaCl-KCl}}^s = \frac{573.04}{T} + 0.17979 - (0.4202E-4)T \quad (9)$$

NaCl-KCl Liquid

The form of equations (4)-(7) remain unchanged for the anhydrous liquid. The expression for the Margules parameters are simpler, as might be expected since the liquid solution departs only slightly from ideality. Pertinent experimental data are given by Hersh and Kleppa (1965), Chou (1982), Pelton et al. (1985), and Chou et al. (1991). The resulting expressions are:

$$w a_{\text{NaCl-KCl}}^l = - \frac{246.60}{T} - 0.22741 - \frac{0.031026(P-1)}{T} \quad (10)$$

$$w b_{\text{NaCl-KCl}}^l = - \frac{32.70}{T} + 0.12075 \quad (11)$$

Here the values -246.6 and -32.7 were determined by the heat of mixing data of Hersh and Kleppa.

4. THE NaCl-H₂O AND KCl-H₂O BINARY SYSTEMS

No solid solution exists in either the NaCl-H₂O or KCl-H₂O binary system, so the chemical potential of the crystalline solid in equilibrium with either binary aqueous solution at any temperature and pressure is equal to the reference potential. For either liquid, however, the behavior over the full composition range from solid saturation to pure H₂O is complex and involves vapor-liquid phase separation below the critical pressure for a given temperature. As noted above, two treatments have been published, each of which is valid over a substantial but still incomplete range of composition in the high temperature range of current interest (Pitzer and Li, 1983; Tanger and Pitzer, 1989). While each of these fitted solid solubility at the three-phase pressure, neither considered this solubility at higher pressures.

For this project we chose a very simple equation which is adequate for the representation of the chemical potential of the salt at saturation composition at various pressures. This is a single term Margules expression, i.e., of the same form as eq. (6) without the $w b$ term.

$$\mu_{\text{aq},P,T}^{\text{MCl}} = \mu_{i,P,T}^{\text{MCl}} + RT \ln x_{\text{MCl}} + RT \ln \gamma_{\text{MCl}} \quad (12)$$

$$\ln \gamma_{\text{MCl}} = x_{\text{H}_2\text{O}}^2 w_{\text{MCl-H}_2\text{O}}^i \quad (13)$$

Currently available data (Gunter et al., 1983; Chou, 1987; Chou et al., 1991) for the two aqueous binaries were regressed, yielding the results

$$w_{\text{NaCl-H}_2\text{O}}^i = -\frac{600.08}{T} + 0.60794 - \frac{0.12920(P-1)}{T} \quad (14)$$

$$w_{\text{KCl-H}_2\text{O}}^i = -\frac{781.42}{T} + 0.39498 - \frac{0.15446(P-1)}{T} \quad (15)$$

In all calculations, $R = 8.31447 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$.

5. THE NaCl-KCl-H₂O TERNARY SYSTEM

The NaCl-KCl-H₂O ternary system exhibits both solid solution between NaCl and KCl and liquid miscibility between all three components in the range of present interest. Thus, the chemical potential of each component in either the crystal or the liquid phase is composition-dependent as well as a function of pressure and temperature. It is convenient to write first the molal excess Gibbs energy for the ternary. This comprises just the terms from the three binaries plus one ternary composition, triple interaction parameter.

$$\begin{aligned} g^{\text{ex}}/RT = & x_{\text{H}_2\text{O}} (x_{\text{NaCl}} w_{\text{NaCl-H}_2\text{O}}^i + x_{\text{KCl}} w_{\text{KCl-H}_2\text{O}}^i) \\ & + x_{\text{NaCl}} x_{\text{KCl}} (w_{\text{NaCl-KCl}}^i + x_{\text{NaCl}} w_{\text{NaCl-KCl}}^i + x_{\text{H}_2\text{O}} w_{\text{NaCl-KCl-H}_2\text{O}}^i) \end{aligned} \quad (16)$$

After adding the terms for ideal mixing and for the reference states and conversion to the total Gibbs energy, the standard differentiations yield the chemical potentials and thereby the activity coefficients. Equations (4), (5), and (12) still apply, but the activity coefficients now become

$$\begin{aligned} \ln \gamma_{\text{NaCl}}^i = & + x_{\text{H}_2\text{O}} (1 - x_{\text{NaCl}}) w_{\text{NaCl-H}_2\text{O}}^i - x_{\text{KCl}} x_{\text{H}_2\text{O}} w_{\text{KCl-H}_2\text{O}}^i \\ & + x_{\text{KCl}} (1 - x_{\text{NaCl}}) (w_{\text{NaCl-KCl}}^i + 2x_{\text{NaCl}} w_{\text{NaCl-KCl}}^i) \\ & + x_{\text{KCl}} x_{\text{H}_2\text{O}} (1 - 2x_{\text{NaCl}}) w_{\text{NaCl-KCl-H}_2\text{O}}^i \end{aligned} \quad (17)$$

$$\begin{aligned} \ln \gamma_{\text{KCl}}^i = & - x_{\text{NaCl}} x_{\text{H}_2\text{O}} w_{\text{NaCl-H}_2\text{O}}^i + (1 - x_{\text{KCl}}) w_{\text{KCl-H}_2\text{O}}^i x_{\text{H}_2\text{O}} \\ & + x_{\text{NaCl}} (1 - x_{\text{KCl}}) w_{\text{NaCl-KCl}}^i + x_{\text{NaCl}}^2 (1 - 2x_{\text{KCl}}) w_{\text{NaCl-KCl}}^i \end{aligned}$$

$$+ x_{\text{NaCl}} x_{\text{H}_2\text{O}} (1 - 2x_{\text{KCl}}) w_{\text{NaCl-KCl-H}_2\text{O}}^{\dagger} \quad (18)$$

One notes that if any one mole fraction is set to zero, these equations reduce to those given above for the binaries. Measurements were made by Chou et al. (1991) for the liquid compositions in this ternary. The overall regression described below yields the binary parameters given previously and the following expression for the ternary composition, triple interaction parameter

$$w_{\text{NaCl-KCl-H}_2\text{O}}^{\dagger} = \frac{392.62}{T} - 0.61532 + \frac{0.15223(P-1)}{T} \quad (19)$$

6. FITTING PROCEDURE

The coefficients of the Margules expansions used to describe the excess Gibbs energy of mixing in the liquid or solid phase in the NaCl-KCl-H₂O ternary and its subsystems were evaluated using a global, non-linear, least-squares optimization procedure. The main advantage of the non-linear approach is that it permits more flexibility in the types of data used in the regression. In the present exercise, only a portion of the data set was amenable to direct linear regression (specifically, the liquidus data in the NaCl-H₂O and KCl-H₂O binaries and the solvus data in the NaCl-KCl system). The remainder of the PTX data could not be incorporated directly into a linear least-squares fit. The main disadvantage to the non-linear approach is that it is very computer-intensive. Because many of the thermodynamic relationships involved cannot be solved explicitly in terms of the Margules coefficients, each step in the regression involves solving the appropriate chemical potential equalities numerically.

Temperature was selected as the dependent variable in our fitting procedure and the quantity $\Sigma(T^{\text{obs}} - T^{\text{calc}})^2$ was minimized. Earlier fitting attempts used composition as the dependent variable. This practice was abandoned due to complications arising from undefined solutions near the invariant points. The PTX data used in the regression have been cited above and are tabulated in Chou et al. (1991).

For each type of data used in the regression, the appropriate equations (the simultaneous equality of chemical potentials of NaCl and/or KCl between phases) were solved numerically for temperature at the experimental P-X conditions. Thus, an initial set of values for the coefficients was required to begin the procedure. The initial values of the parameters for the NaCl-H₂O and KCl-H₂O binaries were derived by linear regression with Gibbs energy as the dependent variable. Both sets of coefficients were then re-optimized using the T-dependent non-linear procedure. The phase diagram calculated using the new coefficients more accurately reproduced the experimental liquidus data in each binary system.

Starting parameters for the asymmetric Margules expansion for the NaCl-KCl binary were derived using compositions of coexisting phases on the solvus and approximate compositions and temperatures of the minimum melting points at different pressures (Pelton et al., 1985). Unfortunately, this procedure permits the inclusion of only these rather specialized data points for which the compositions of both phases present in equilibrium are known at the same P and T. During the non-linear regression these initial

coefficients changed considerably with the addition of the rest of the NaCl-KCl liquidus and solidus data.

Once satisfactory values for the P-T dependences of the Margules coefficients for the individual binaries were obtained, the NaCl-KCl-H₂O ternary liquidus data were included in the regression, but only the NaCl-KCl binary coefficients were allowed to vary (the coefficients for the NaCl-H₂O and KCl-H₂O binaries were held at the previous values). Although the coefficients derived from separate fits to the individual binaries provided a reasonably accurate phase diagram for the ternary system, the simultaneous regression of both the ternary and NaCl-KCl binary data resulted in notable improvement within the ternary at little expense to the goodness of fit in the NaCl-KCl binary. Finally, it was found that with one additional Margules term (and its P-T dependences) representing ternary composition, three-particle interactions, the resulting phase diagram predicted the ternary liquidus within experimental uncertainty.

7. RESULTS AND DISCUSSION

Figure 1a shows the NaCl-KCl binary phase diagrams at 1 bar for both liquid and solid with experimental points included. One notes that the KCl-rich side shows less departure from ideality than the NaCl side for both liquid and solid. This is expected since a smaller ion fits more easily into a pattern dominated by larger ions than vice versa. Figure 1b shows the same diagrams for 5000 bars; one notes the substantial increases in temperature caused by the pressure change. At intermediate pressures the agreement with experiment is similar to that shown for these two pressures.

While the heat of mixing for liquid NaCl-KCl was known from Hersh and Kleppa (1965), the comprehensive table of Pelton (1988) shows no value for the entropy of mixing. Our results in equations (10) and (11) yield for the excess entropy:

$$S^{ex}/R = 0.227 - 0.121x_{NaCl} \quad (20)$$

For an equimolal mixture this indicates that both the enthalpy and excess entropy contributions to the Gibbs energy of mixing are negative, which is a relatively unusual pattern. The recent tabulation of Pelton (1988) shows that most fused salt systems have negative enthalpy of mixing, but the excess entropy is also negative, which yields a positive contribution to ΔG . Both LiOH-NaOH and NaOH-KOH, however, have the same qualitative pattern as we find for NaCl-KCl.

Figure 2 shows the diagram for the ternary liquid at two pressures. The experimental data are shown with agreement to better than 8° in all cases and much better for most points. At lower temperatures the isotherms show a sharp change in slope at the cotectic where there are two different solids in equilibrium. At higher temperatures the curves are continuous with a single solid solution phase.

For the aqueous systems, our equations are valid above about 673 K, which is the range of experimental data here considered. There are data and equations now available for lower temperatures; hence, it did not seem worthwhile to complicate our present treatment. The limitation of the aqueous equations to the solid saturation surface was discussed above. With increase of temperature the equations are valid to the melting points of the pure salts. While the primary experimental data for the aqueous

systems extend only to 2000 bars, they show no significant departure from linear pressure dependence. Thus, we believe extrapolation to 5 kbar is reasonable. For the solid there are data to much higher pressures and these show closely linear dependence. Also, there is no lower limit of temperature for the validity of the equation for the solids; it shows a smooth trend to pure solid compositions with decrease in T.

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FIGURE CAPTIONS

Figure 1. Phase relations in the NaCl-KCl anhydrous binary system at 1 and 5000 bars calculated as outlined in the text. Circles are liquidus data from Chou (1981), solidus data from Chou et al. (1991), and solvus data at 1 bar from Barrett and Wallace (1954) and Vesnina and Zakovryashin (1979) and at higher pressures from Bhardwaj and Roy (1971).

Figure 2. Isobaric projections of the liquidi in the NaCl-KCl-H₂O ternary system at 500 and 2000 bars calculated as outlined in the text. Circles are liquidus data from Chou (1981), Gunter et al. (1983) and Chou et al. (1991). The diameter of each circle shows the difference between experimental liquidus temperatures and those calculated using our model. Open circles mean that predicted temperatures are lower than observed and filled circles indicate predicted temperatures are higher.

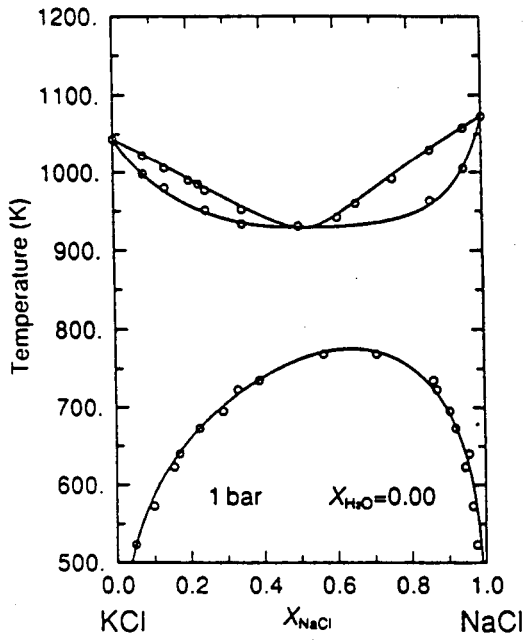


Fig. 1a

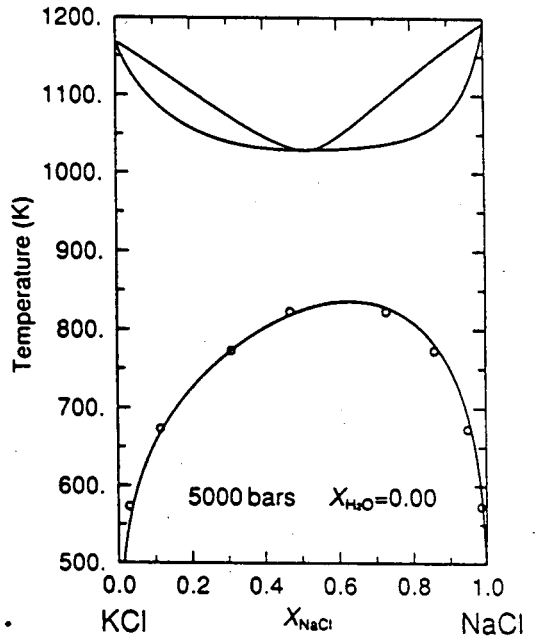


Fig. 1b

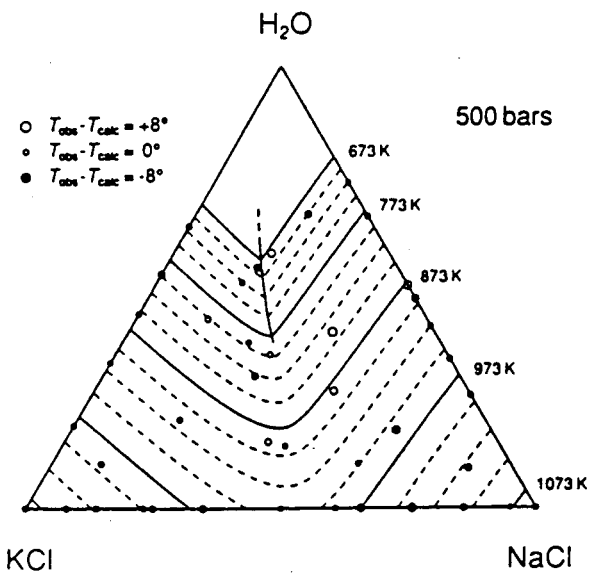


Fig. 2a

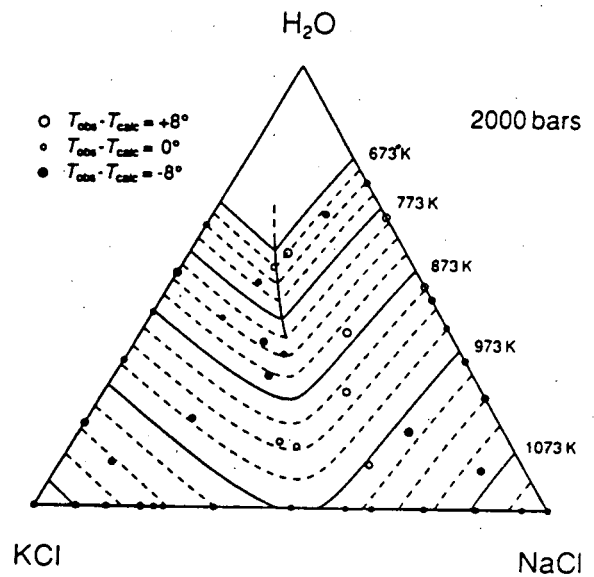


Fig. 2b

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720