

[AMERICAN JOURNAL OF SCIENCE, VOL. 269, NOVEMBER 1970, P. 402-413]

FUGACITIES AND ACTIVITY COEFFICIENTS OF NaCl IN NaCl-H₂O FLUIDS AT ELEVATED TEMPERATURES AND PRESSURES

THOMAS R. WELLMAN*

Department of Geology and Geophysics, Yale University,
New Haven, Connecticut 06520

ABSTRACT. Experimental data for coexisting synthetic nepheline, sodalite, and aqueous fluid have been used to calculate the fugacities and activity coefficients of NaCl in aqueous fluid as a function of temperature, pressure, and NaCl mole fraction in the range 500° to 700°C and 600 to 2000 bars fluid pressure.

INTRODUCTION

Aqueous NaCl rich fluids play an important role in geological processes. Sea water and ground water from many sedimentary basins contain NaCl as the principal dissolved salt. The Salton Sea geothermal waters are essentially aqueous NaCl-CaCl₂-KCl solutions (Helgeson, 1968). Fluid inclusions in both igneous and metamorphic minerals commonly contain concentrated salt solutions. These solutions are sometimes saturated, containing cubic crystals of alkali chloride (Roedder, 1958).

An understanding of the thermodynamics of aqueous alkali chloride solutions at elevated temperature and pressure will prove useful, indeed necessary, to the understanding of metamorphism, hydrothermal alteration and ore deposition, and many types of igneous activity.

NaCl-H₂O phase chemistry at temperatures and pressures up to 700°C and 1500 bars was presented by Sourirajan and Kennedy (1962). Copeland, Silverman, and Benson (1952) have studied the pressure-volume-temperature properties of NaCl-H₂O fluids in the range 380° to 400°C and 210 to 300 atm pressure. Ionization constants for NaCl and KCl in aqueous fluid at several temperatures and pressures are listed by Barnes, Helgeson, and Ellis (1966).

The fugacities, activities, and activity coefficients of undissociated NaCl in NaCl-H₂O fluids have not previously been studied at elevated temperatures and pressures.

The present paper derives these data from the experimental results in the system NaAlSiO₄-KAlSiO₄-NaCl-KCl-H₂O reported by Wellman (1970).

THE FUGACITY OF NaCl OVER SODALITE + NEPHELINE, CRYSTALLINE NaCl, AND HYPOTHETICAL PURE MOLTEN NaCl

The vapor pressure data of Wellman (1969) yield the equation for NaCl fugacity over sodalite plus nepheline:

$$\ln (f_{\text{NaCl}}^{\text{So}+\text{Ne}})_{P=0} = + 25.516 - 43.523(1000/T)$$

where $(f_{\text{NaCl}}^{\text{So}+\text{Ne}})_{P=0}$ is the fugacity in bars at zero solid pressure and T is in °K.

* Present address: TN73/Geochemistry Branch, NASA Manned Spacecraft Center, Houston, Texas 77058

JAN 25 1971

The data of Zimm and Mayer (1944), Mayer and Wintner (1938), and Kelley (1935) for the vapor pressure of crystalline NaCl may be described by the least squares fitted equation:

$$\ln (f_{\text{NaCl}}^{\text{XI}})_{P=0} = 16.0633 - 25.6467 (1000/T)$$

where $(f_{\text{NaCl}}^{\text{XI}})_{P=0}$ is the fugacity of NaCl over crystalline NaCl in bars at zero solid pressure and T is in $^{\circ}\text{K}$.

Now, for hypothetical molten NaCl:

$$\ln (f_{\text{NaCl}}^{\text{L}})_{P=0} = \frac{H_{\text{NaCl}}^{\text{F}}}{R} \left(\frac{1000}{T} - \frac{1000}{T_{\text{NaCl}}^{\text{F}}} \right) + \ln (f_{\text{NaCl}}^{\text{XI}})_{P=0}$$

where $(f_{\text{NaCl}}^{\text{L}})_{P=0}$ is the fugacity of hypothetical pure molten NaCl at zero pressure on the liquid, $H_{\text{NaCl}}^{\text{F}}$ is the heat of fusion of NaCl in kcal/mole, assumed independent of temperature, and $T_{\text{NaCl}}^{\text{F}}$ is the NaCl fusion temperature (1073°K or 800°C).

According to Wicks and Block (1963), $H_{\text{NaCl}}^{\text{F}} = 6.850$ kcal/mole. Substituting:

$$\ln (f_{\text{NaCl}}^{\text{L}})_{P=0} = 12.8513 - 22.1997 (1000/T)$$

where T is in $^{\circ}\text{K}$.

Figure 1 is a natural logarithm fugacity versus $1000/T$ plot showing the relationship of the various fugacities.

To correct for pressure on the condensed phase(s), we may use the equation:

$$\ln f_{\text{NaCl}}^* = \ln (f_{\text{NaCl}}^*)_{P=0} - \frac{P_{\text{c}}V_{\text{c}}}{RT} \quad (1)$$

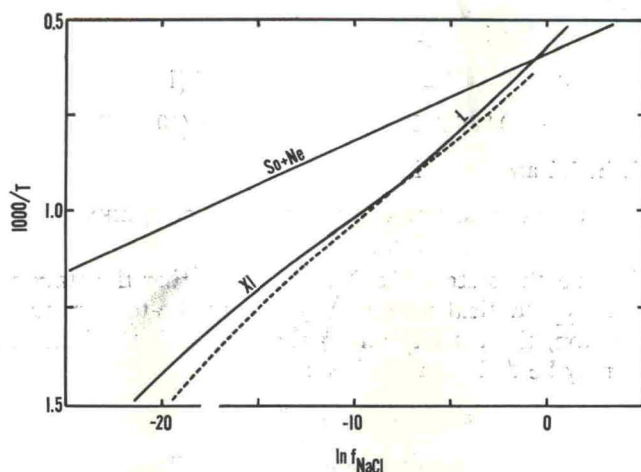


Fig. 1. Plot of log fugacity versus $1000/T^{\circ}\text{K}$ showing the curves for $f_{\text{NaCl}}^{\text{So+Ne}}$ (indicated by So+Ne), $f_{\text{NaCl}}^{\text{XI}}$ (indicated by XI), and $f_{\text{NaCl}}^{\text{L}}$ (indicated by L). The dashed curves are metastable extensions.

where * is a general superscript which can represent $^{So+Ne}$, ^{X1} or ^{L} , P_C is the pressure on the condensed phase(s), $V_{C\rightarrow}$ is the condensed phase volume of reaction, T is in $^{\circ}K$, and compressibility of the condensed phases has been neglected.

The average cell edge for synthetic starting sodalite is 8.872 ± 0.001 Å, which corresponds to a molar volume of 210.4 cm³. The hydrothermally prepared pure sodium nepheline of Smith and Tuttle (1957) has a cell volume of 718.0 Å³ and a molar volume of 54.1 cm³. Therefore, the condensed phase volume of reaction for the sodalite plus nepheline reaction is -48.1 cm³ at $25^{\circ}C$.

Thermal expansion data reported by Skinner (1966) and Taylor (1968) suggest that for the sodalite plus nepheline reaction in the temperature range of 400 to $800^{\circ}C$:

$$V_{C\rightarrow} = -0.002T - 48.2$$

where T is in $^{\circ}K$, and the volume is in cm³.

Substituting into (1):

$$\ln f_{NaCl}^{So+Ne} = \frac{0.002 P_C}{R} + \frac{48.2 P_C}{RT} - \frac{43523}{T} + 25.516$$

for T (in $^{\circ}K$) between 673 and $1073^{\circ}K$ (400 to $800^{\circ}C$) and P_C in bars to several kilobars.

For the molten NaCl case, the condensed volume of reaction is minus the molar volume of molten NaCl. Taking the volume and thermal expansion of molten NaCl given in Skinner (1966) and assuming the thermal expansion independent of temperature:

$$V_{C\rightarrow} = -25.451 \exp(0.000367 T)$$

where T is in $^{\circ}K$ and $V_{C\rightarrow}$ is in cm³.

Substituting this into (1):

$$\begin{aligned} \ln (f_{NaCl}^L) &= 12.8513 - 22.1997 (1000/T) \\ &+ 0.30610 P_C \exp (0.000367 T) (1000/T) \end{aligned}$$

where T is in $^{\circ}K$ and P_C is in kilobars.

FUGACITY, ACTIVITY, AND ACTIVITY COEFFICIENT OF NaCl IN NaCl-H₂O FLUIDS

Considering the system NaCl-H₂O and letting the standard state of NaCl be the hypothetical pure molten salt at the temperature and pressure in question, the activity and activity coefficient of NaCl in NaCl-H₂O fluids may be defined as follows:

$$\begin{aligned} a_{NaCl}^{\circ} &= f_{NaCl}^{\circ \text{ fluid}} / f_{NaCl}^L \\ \gamma_{NaCl}^{\circ} &= a_{NaCl}^{\circ} / X_{chloride}^{\text{fluid}} \end{aligned}$$

where $X_{chloride}^{\text{fluid}}$ is the mole fraction of chloride in the fluid, and $f_{NaCl}^{\circ \text{ fluid}}$, a_{NaCl}° , and γ_{NaCl}° are the fugacity, activity, and activity coef-

ficient of NaCl in NaCl-H₂O fluid at the temperature, pressure, and $X_{\text{chloride}}^{\text{fluid}}$ in question.

These equations can also be written in logarithmic form:

$$\begin{aligned}\ln a_{\text{NaCl}}^{\circ} &= \ln f_{\text{NaCl}}^{\circ \text{ fluid}} - \ln f_{\text{NaCl}}^{\text{L}} \\ \ln \gamma_{\text{NaCl}}^{\circ} &= \ln a_{\text{NaCl}}^{\circ} - \ln X_{\text{chloride}}^{\text{fluid}}\end{aligned}\quad (2)$$

If sodalite and nepheline coexist with NaCl-H₂O fluid, $f_{\text{NaCl}}^{\circ \text{ fluid}}$ is equal to $f_{\text{NaCl}}^{\text{So}+\text{Ne}}$ at the appropriate temperature and pressure. The data for NaCl-H₂O fluids given in Wellman (1970) allow the calculation of one point on a $f_{\text{NaCl}}^{\circ \text{ fluid}}$ (or a_{NaCl}°) versus $X_{\text{chloride}}^{\text{fluid}}$ curve for each temperature and pressure at which experiments were performed.

However, making certain assumptions concerning the nature of Na-K mixing in aqueous chloride fluids, sodalite solid solution, and nepheline solid solution (see below), additional $f_{\text{NaCl}}^{\circ \text{ fluid}}$ values may be derived from the data for coexisting sodalite, nepheline, and aqueous chloride fluid in the K-bearing system given by Wellman (1970).

THE ACTIVITY OF NaAlSiO₄ IN NEPHELINE SOLID SOLUTION

The activities of Na and K will be assumed unity in the pure Na and K nepheline end-members, respectively, at the temperature and pressure in question. Activities of Na and K will also be set to unity in pure NaCl-H₂O and KCl-H₂O fluids at the temperature, pressure, and total chloride mole fraction ($X_{\text{chloride}}^{\text{fluid}}$) of the fluid in question.

The total exchange reaction between nepheline and fluid is:



where the superscripts ^{Ne} and ^{fluid} indicate nepheline and fluid, respectively.

By definition:

$$K_{\text{Ne}} = \frac{a_{\text{NaCl}}^{\text{fluid}} a_{\text{Ks}}^{\text{Ne}}}{a_{\text{KCl}}^{\text{fluid}} a_{\text{Ne}}^{\text{Ne}}}$$

where $a_{\text{Ne}}^{\text{Ne}}$ and $a_{\text{Ks}}^{\text{Ne}}$ are the activities of Na and K nepheline end-members in nepheline solid solution, and $a_{\text{NaCl}}^{\text{fluid}}$ and $a_{\text{KCl}}^{\text{fluid}}$ are the activities of NaCl and KCl in the fluid, respectively.

Nepheline (and sodalite) are only slightly soluble in the fluid over the temperature and pressure range dealt with in this study (Wellman, 1970). This solubility will be assumed to have no effect upon the properties of the aqueous chloride fluid.

Assuming that Na and K mix ideally in the aqueous chloride fluid:

$$a_{\text{KCl}}^{\text{fluid}}/a_{\text{NaCl}}^{\text{fluid}} = X_{\text{KCl}}^{\text{chloride}}/X_{\text{NaCl}}^{\text{chloride}}$$

where $X_{\text{KCl}}^{\text{chloride}}$ and $X_{\text{NaCl}}^{\text{chloride}}$ are equal to the mole ratios KCl/NaCl+KCl and NaCl/NaCl+KCl, respectively, in the fluid.

Substituting back:

$$a_{\text{Ks}}^{\text{Ne}} = a_{\text{Ne}}^{\text{Ne}} K_{\text{Ne}}^z \quad (3)$$

where $z = X_{\text{KCl}}^{\text{chloride}}/X_{\text{NaCl}}^{\text{chloride}}$.

It should be noted that the assumption of ideal mixing of Na and K in the fluid implies that NaCl and KCl interact in the same way with H₂O. That this might, in fact, be approximately true is suggested by the gross similarity of the three phase and saturation curves in the NaCl-H₂O and KCl-H₂O systems (Sourirajan and Kennedy, 1962; Keevil, 1942; Benedict, 1939; and Benrath and others, 1937) and (somewhat circularly) by the internal consistency of the data presented in this paper. It cannot, however, be considered as proved, and users of these data are cautioned to keep the somewhat arbitrary nature of this assumption in mind.

Now, from the Gibbs-Duhem equation:

$$X_{\text{Ne}}^{\text{Ne}} d(\ln a_{\text{Ne}}^{\text{Ne}}) = -X_{\text{Ks}}^{\text{Ne}} d(\ln a_{\text{Ks}}^{\text{Ne}})$$

where $X_{\text{Ne}}^{\text{Ne}}$ and $X_{\text{Ks}}^{\text{Ne}}$ are the mole fractions of Na and K end-members in nepheline solid solution, respectively.

Substituting (3) into the above and differentiating:

$$X_{\text{Ne}}^{\text{Ne}} d(\ln a_{\text{Ne}}^{\text{Ne}}) = -X_{\text{Ks}}^{\text{Ne}} d(\ln a_{\text{Ne}}^{\text{Ne}} + \ln K_{\text{Ne}} + \ln z)$$

$$X_{\text{Ne}}^{\text{Ne}} + X_{\text{Ks}}^{\text{Ne}} = -X_{\text{Ks}}^{\text{Ne}} \left(\frac{d(\ln z)}{d(\ln a_{\text{Ne}}^{\text{Ne}})} \right) = 1$$

$$d(\ln a_{\text{Ne}}^{\text{Ne}}) = -X_{\text{Ks}}^{\text{Ne}} d(\ln z)$$

Integrating:

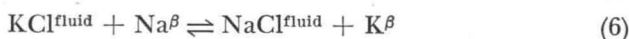
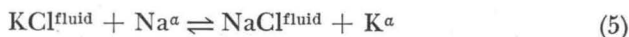
$$\ln a_{\text{Ne}}^{\text{Ne}} = -\int X_{\text{Ks}}^{\text{Ne}} d(\ln z) \quad (4)$$

The non-logarithmic form of this equation can be integrated graphically from experimental data for coexisting nepheline solid solution and fluid. This method has the advantage of requiring no a priori assumptions concerning the nature of the nepheline solid solution. However, because the necessary data in the K poor part of the system are not available, a model will be fit to the experimental data to allow extrapolation to $z = 0$.

Nepheline has two crystallographically, and presumably energetically, distinct alkali cation sites (Buerger, Klein, and Donnay, 1954; Hahn and Buerger, 1955). These sites occur in the ratio of one large site, which preferentially accepts K, to three small sites which preferentially accept Na.

It is therefore logical to apply the model, developed by Grover and Orville (1969), that assumes the coexistence of a one site ideal mixture phase with a phase possessing two distinct crystallographic sites, each of which behaves as an ideal mixture.

Two exchange reactions may be written, one between the aqueous fluid and each crystallographically distinct cation site in nepheline:



where α represents the large K-preferring site, β represents the smaller Na-preferring sites, and fluid represents fluid.

Standard states for K in α and β and Na in α and β are pure KAlSiO₄ and NaAlSiO₄ end-members, respectively, at the temperature and pressure in question. The standard states for NaCl^{fluid} and KCl^{fluid} are the pure NaCl-H₂O and KCl-H₂O fluids, respectively, at the temperature, pressure, and $X_{\text{chloride}}^{\text{fluid}}$ of the actual aqueous fluid.

The standard state Gibbs free energies for reactions (5) and (6) are:

$$G^{\circ}_{1 \rightarrow} = -RT \ln \frac{a_K^{\alpha} a_{\text{NaCl}}^{\text{fluid}}}{a_{\text{KCl}}^{\text{fluid}} a_{\text{Na}}^{\alpha}}$$

$$G^{\circ}_{2 \rightarrow} = -RT \ln \left(\frac{a_K^{\beta} a_{\text{NaCl}}^{\text{fluid}}}{a_{\text{KCl}}^{\text{fluid}} a_{\text{Na}}^{\beta}} \right)$$

where the subscripts ₁ and ₂ refer to reactions (5) and (6), respectively, and a_K^{α} , a_{Na}^{α} , a_K^{β} , and a_{Na}^{β} are the activities of K in site α , Na in site α , K in site β , and Na in site β , respectively.

From the assumption of ideal mixtures:

$$G^{\circ}_{1 \rightarrow} = -RT \ln \left(\frac{X_K^{\alpha} X_{\text{NaCl}}^{\text{chloride}}}{X_{\text{KCl}}^{\text{chloride}} X_{\text{Na}}^{\alpha}} \right)$$

$$G^{\circ}_{2 \rightarrow} = -RT \ln \left(\frac{X_K^{\beta} X_{\text{NaCl}}^{\text{chloride}}}{X_{\text{KCl}}^{\text{chloride}} X_{\text{Na}}^{\beta}} \right)$$

where X_K^{α} , X_{Na}^{α} , X_K^{β} , and X_{Na}^{β} are the mole fractions of K in site α , Na in site α , K in site β , and Na in site β , respectively.

Solving for X_K^{α} and X_K^{β} :

$$X_K^{\alpha} = \frac{X_{\text{KCl}}^{\text{chloride}} K_{\alpha}}{X_{\text{KCl}}^{\text{chloride}} K_{\alpha} - X_{\text{KCl}}^{\text{chloride}} + 1} \quad (7)$$

$$X_K^{\beta} = \frac{X_{\text{KCl}}^{\text{chloride}} K_{\beta}}{X_{\text{KCl}}^{\text{chloride}} K_{\beta} - X_{\text{KCl}}^{\text{chloride}} + 1} \quad (8)$$

where $K_{\alpha} = \exp(-G^{\circ}_{1 \rightarrow}/RT)$ and $K_{\beta} = \exp(-G^{\circ}_{2 \rightarrow}/RT)$.

From the ratio of the number of sites, $X_{\text{Ks}}^{\text{Ne}}$, the mole fraction KAlSiO₄ in nepheline solid solution, is defined as:

$$X_{\text{Ks}}^{\text{Ne}} = (X_K^{\alpha} + 3X_K^{\beta})/4 \quad (9)$$

Unfortunately, $G^{\circ}_{1 \rightarrow}$ and $G^{\circ}_{2 \rightarrow}$ cannot be expressed explicitly in terms of $X_{\text{KCl}}^{\text{chloride}}$ and $X_{\text{Ks}}^{\text{Ne}}$. In this study, $G^{\circ}_{1 \rightarrow}$ and $G^{\circ}_{2 \rightarrow}$ were chosen by an iterative computer method to minimize the squared deviations between observed and calculated values of $X_{\text{Ks}}^{\text{Ne}}$. Equations (7) and (8) substituted into (9) were used to calculate the $X_{\text{Ks}}^{\text{Ne}}$ values.

The application of the least squares method to the data of Wellman (1970) for coexisting nepheline solid solution and aqueous fluid yield the following energy values:

$$G^{\circ}_{1 \rightarrow} = -2.5 \pm 0.5 \text{ kcal/mole}$$

$$G^{\circ}_{2 \rightarrow} = 6.0 \pm 0.8 \text{ kcal/mole}$$

Substituting the formula for X_{Ks}^{Ne} into (4):

$$\ln a_{Ne}^{Ne} = -\frac{K_a}{4} \int \frac{z}{K_a z + 1} d(\ln z) - \frac{3K_\beta}{4} \int \frac{z}{K_\beta z + 1} d(\ln z)$$

And, integrating:

$$\ln a_{Ne}^{Ne} = -\left. \frac{\ln(K_a z + 1) + 3\ln(K_\beta z + 1)}{4} \right|_{z=0}^z$$

Noting that $\ln a_{Ne}^{Ne} = 0$ ($a_{Ne}^{Ne} = 1$) when $z = 0$ (pure Na system):

$$\ln a_{Ne}^{Ne} = -\frac{\ln(K_a z + 1) + 3\ln(K_\beta z + 1)}{4} \quad (10)$$

Activities calculated from this formula agree, over the range of available data, with those derived from graphical integration of (4), as they must in so far as the model curves fit the data. The two site model, however, not only allows a reasonable extrapolation to the Na end-member standard state but also gives the activities in closed analytic form instead of requiring graphical or numerical integration.

THE ACTIVITY OF Na END-MEMBER IN SODALITE SOLID SOLUTION

The exchange reaction between sodalite solid solution and an aqueous chloride fluid may be written as follows:



where the superscripts ^{fluid} and ^{so} denote the fluid and the sodalite solid solution, respectively.

The standard states for Na^{so} and K^{so} are defined as pure Na and K sodalite end-members, respectively, at the temperature and pressure of the reaction. Na^{fluid} and K^{fluid} standard states are as defined previously.

By definition of the equilibrium constant (K_{so}) and the standard state Gibbs free energy ($G^\circ_{so \rightarrow}$) of the above reaction:

$$K_{so} = \exp(-G^\circ_{so \rightarrow}/RT) = (a_{Po}^{so} a_{NaCl}^{fluid} / a_{KCl}^{fluid} a_{so}^{so})$$

where a_{so}^{so} and a_{Po}^{so} are the activities of Na and K sodalite end-members, respectively, in sodalite solid solution.

Assuming, as before, that Na and K mix ideally in the fluid, and further assuming that Na and K sodalite end-members mix ideally in the sodalite solid solution:

$$K_{so} = \exp(-G^\circ_{so \rightarrow}/RT) = X_{Po}^{so} / X_{so}^{so} \quad (11)$$

And:

$$\ln a_{so}^{so} = \ln X_{so}^{so} = -\ln(K_{so} z + 1) \quad (12)$$

where X_{so}^{so} and X_{Po}^{so} are the mole fractions of Na and K sodalite end-members in sodalite solid solution.

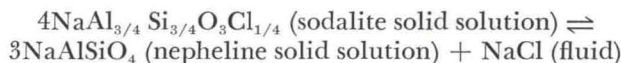
The data of Wellman (1970) involve sodalites with no more than 8 mole percent K end-member. Therefore, even if not strictly valid at all compositions, the assumption of ideal Na-K mixing in sodalite solid solution should be useful in this limited composition range.

The application of equation (11) to the data of Wellman (1970) for coexisting sodalite solid solution and fluid yields a mean value and mean deviation for the Gibbs free energy of:

$$G^{\circ}_{\text{So}} \rightarrow = 5.47 \pm 0.18 \text{ kcal/mole}$$

FUGACITY OF NaCl FROM NaCl-KCl-H₂O FLUID DATA

For the Na-bearing components involved in the decomposition of sodalite:



where the coefficients have been chosen to keep the total number of moles constant.

The equilibrium constant is:

$$K_D = \frac{f_{\text{NaCl}}^{\text{fluid}} (a_{\text{Ne}}^{\text{Ne}})^3}{(a_{\text{So}}^{\text{So}})^4}$$

Now, when $X_{\text{So}}^{\text{So}}$ and $X_{\text{Ne}}^{\text{Ne}}$ equal unity (pure Na system):

$$K_D = f_{\text{NaCl}}^{\text{So}+\text{Ne}}$$

$f_{\text{NaCl}}^{\text{So}+\text{Ne}}$ being taken at the appropriate temperature and pressure.

Substituting and rearranging:

$$f_{\text{NaCl}}^{\text{fluid}} = \left(\frac{(a_{\text{So}}^{\text{So}})^4}{(a_{\text{Ne}}^{\text{Ne}})^3} \right) f_{\text{NaCl}}^{\text{So}+\text{Ne}}$$

Substituting (10) and (12) into the above equation:

$$\begin{aligned} \ln f_{\text{NaCl}}^{\text{fluid}} &= \frac{3}{4} \ln(K_{\alpha z} + 1) + \frac{9}{4} \ln(K_{\beta z} + 1) \\ &\quad - 4 \ln(K_{\text{So}z} + 1) + \ln f_{\text{NaCl}}^{\text{So}+\text{Ne}} \end{aligned} \quad (13)$$

$\ln f_{\text{NaCl}}^{\text{fluid}}$ may be calculated for any point in the K-bearing system at which sodalite, nepheline, and fluid coexist.

From the assumption that $a_{\text{NaCl}}^{\text{fluid}} = \text{unity}$ when $X_{\text{KCl}}^{\text{chloride}} = 0$, and from the assumption of ideal Na-K mixing in the fluid:

$$a_{\text{NaCl}}^{\text{fluid}} = 1 - X_{\text{KCl}}^{\text{chloride}}$$

And:

$$\begin{aligned} f_{\text{NaCl}}^{\text{fluid}} &= (1 - X_{\text{KCl}}^{\text{chloride}}) f_{\text{NaCl}}^{\circ \text{ fluid}} \\ f_{\text{NaCl}}^{\circ \text{ fluid}} &= f_{\text{NaCl}}^{\text{fluid}} / (1 - X_{\text{KCl}}^{\text{chloride}}) \end{aligned} \quad (14)$$

APPLICATION TO THE DATA FOR COEXISTING NEPHELINE, SODALITE,
AND AQUEOUS CHLORIDE FLUID

The data of Wellman (1970) include 56 experimental runs which involve nepheline, sodalite, and aqueous chloride fluid, including only points at which both nepheline and sodalite are major phases.

If it is assumed that NaCl and KCl mix ideally in the aqueous fluid, that sodalite is an ideal solid solution of Na and K end-members, and that the nepheline obeys the two-site ideal solution model of Grover and Orville (1969) in Na and K, then, given temperature, pressure, $K/(Na+K)$ in the fluid ($X_{KCl}^{chloride}$), and chloride mole fraction in the fluid ($X_{chloride}^{fluid}$) for each experimental point, one may calculate the natural log of NaCl fugacity in the fluid ($\ln f_{NaCl}^{fluid}$) from equation (13), the natural log of NaCl fugacity in NaCl-H₂O fluid at the same $X_{chloride}^{fluid}$ ($\ln f_{NaCl}^{\circ fluid}$) from equation (14), and the natural log (and $\log_{10}$) of the activity coefficient of NaCl in NaCl-H₂O fluid with respect to NaCl liquid ($\ln \gamma_{NaCl}^{\circ}$) from equation (2). These data are given in table 1.

The following equation was fitted to the data of table 1 by a computerized least squares procedure:

$$\begin{aligned} \ln \gamma_{NaCl}^{\circ} = & 20.898 - 29.279 (1000/T) + 0.0476 (\ln X_{chloride}^{fluid}) \\ & + 4.165 (1000/T)^2 - 0.425 (1000/T) (P) \\ & + 0.0652 (\ln X_{chloride}^{fluid})^2 \end{aligned} \quad (15)$$

where T is in °K, and P is in kilobars.

Figures 2 and 3 show contoured surfaces of $\log_{10} \gamma_{NaCl}^{\circ}$ on a $\log X_{chloride}^{fluid}$ versus $1000/T$ plot at 1000 and 2000 bars. The contours

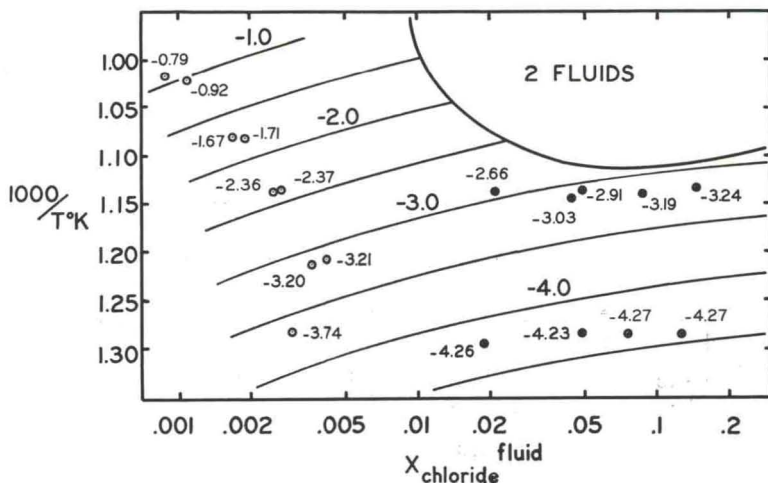


Fig. 2. The contoured surface of $\log_{10} \gamma_{NaCl}^{\circ}$ on a $\log X_{chloride}^{fluid}$ versus $1000/T^{\circ}K$ plot for 1000 bars fluid pressure, generated from equation 15. The extent of the two fluid region is from Sourirajan and Kennedy (1962). The 1000 bar data are included for comparison. Open circles are data from experiments in the NaCl-H₂O system, and filled circles are data from experiments in the NaCl-KCl-H₂O system.

TABLE 1

Observed and calculated values for coexisting
nephelines-sodalite-aqueous fluid data

T°C	P bars	X _{KCl} ^{chloride}	X _{chloride} ^{fluid}	ln f _{NaCl} ^{fluid}	ln f _{NaCl} ^{fluid}	ln γ _{NaCl} [°]	log ₁₀ γ _{NaCl} [*]
501	628	0.000	0.00196	-30.22	-30.22	-8.49	-3.69
503	627	0.000	0.00272	-30.08	-30.08	-8.75	-3.80
502	604	0.699	0.145	-28.40	-27.20	-9.81	-4.26
507	1013	0.000	0.00303	-29.49	-29.49	-8.62	-3.74
501	1000	0.213	0.019	-29.30	-29.06	-9.80	-4.26
507	1020	0.421	0.048	-28.38	-27.84	-9.73	-4.23
506	1030	0.513	0.075	-28.24	-27.52	-9.83	-4.27
506	1030	0.624	0.126	-27.99	-27.01	-9.84	-4.27
501	1476	0.000	0.00818	-29.56	-29.56	-9.71	-4.22
502	1508	0.000	0.01008	-29.47	-29.47	-9.87	-4.29
503	2000	0.000	0.01233	-29.02	-29.02	-9.92	-4.31
505	1978	0.000	0.01590	-28.89	-28.89	-10.11	-4.39
503	1978	0.258	0.061	-28.29	-27.99	-10.49	-4.55
502	1978	0.372	0.093	-28.10	-27.64	-10.51	-4.57
501	1984	0.516	0.145	-27.84	-27.12	-10.41	-4.52
555	600	0.000	0.00041	-26.60	-26.60	-5.15	-2.24
557	604	0.000	0.00045	-26.47	-26.47	-5.18	-2.25
551	1019	0.000	0.00363	-26.55	-26.55	-7.36	-3.20
554	1018	0.000	0.00415	-26.36	-26.36	-7.40	-3.21
552	1510	0.000	0.00798	-26.13	-26.13	-8.01	-3.48
554	1507	0.000	0.00942	-26.01	-26.01	-8.11	-3.52
553	2016	0.000	0.01695	-25.70	-25.70	-8.62	-3.74
554	2010	0.000	0.01701	-25.64	-25.64	-8.59	-3.73
603	600	0.000	0.00035	-23.75	-23.75	-3.59	-1.56
604	604	0.000	0.00041	-23.69	-23.69	-3.72	-1.62
604	1019	0.000	0.00248	-23.40	-23.40	-5.44	-2.36
606	1018	0.000	0.00268	-23.29	-23.29	-5.46	-2.37
606	1009	0.388	0.021	-22.39	-21.90	-6.12	-2.66
599	992	0.409	0.044	-22.74	-22.22	-6.97	-3.03
607	1007	0.451	0.049	-22.21	-21.61	-6.71	-2.91
603	992	0.465	0.087	-22.41	-21.78	-7.33	-3.19
607	1031	0.525	0.140	-22.04	-21.30	-7.46	-3.24
604	1510	0.000	0.00736	-23.07	-23.07	-6.43	-2.79
605	1507	0.000	0.00791	-23.01	-23.01	-6.47	-2.81
608	2008	0.000	0.01821	-22.51	-22.51	-7.12	-3.09
605	2015	0.000	0.01919	-22.67	-22.67	-7.25	-3.15
603	1980	0.110	0.033	-22.50	-22.38	-7.44	-3.23
603	1980	0.224	0.069	-22.23	-21.98	-7.77	-3.38
602	1977	0.306	0.100	-22.11	-21.75	-7.88	-3.42
601	1984	0.454	0.175	-21.86	-21.25	-7.93	-3.44
652	1000	0.000	0.00174	-20.88	-20.88	-3.84	-1.67
651	1002	0.000	0.00188	-20.93	-20.93	-3.95	-1.71
653	1494	0.000	0.00624	-20.51	-20.51	-5.00	-2.17
654	1528	0.000	0.00701	-20.43	-20.43	-5.09	-2.21
651	1978	0.000	0.01819	-20.29	-20.29	-6.03	-2.62
652	2032	0.000	0.01859	-20.21	-20.21	-6.02	-2.61
710	1000	0.000	0.00087	-18.14	-18.14	-1.81	-0.79
706	1002	0.000	0.00109	-18.32	-18.32	-2.12	-0.92
709	988	0.477	0.037	-17.22	-16.57	-3.97	-1.72
705	1017	0.472	0.076	-17.39	-16.75	-4.78	-2.08
705	1017	0.465	0.185	-17.40	-16.77	-5.70	-2.47
703	1494	0.000	0.00526	-18.15	-18.15	-3.68	-1.60
708	1528	0.000	0.00572	-17.90	-17.90	-3.65	-1.58
705	2032	0.000	0.02053	-17.73	-17.73	-4.91	-2.13
700	2000	0.194	0.070	-17.53	-17.31	-5.59	-2.43
702	2012	0.293	0.152	-17.24	-16.89	-6.00	-2.60

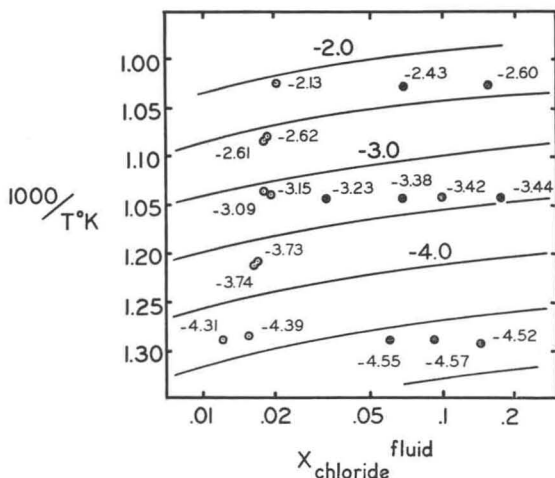


Fig. 3. The contoured surface of $\log_{10} \text{NaCl } \gamma^\circ$ on a $\log X_{\text{chloride}}^{\text{fluid}}$ versus $1000/T^\circ\text{K}$ plot for 2000 bars fluid pressure, generated from equation (15). The 2000 bar data are included for comparison. Open and filled circles have the same significance as in figure 2.

were generated from equation (15). The extent of the two fluid region at 1000 bars was obtained from the work of Sourirajan and Kennedy (1962). The two fluid region was not encountered between 500° and 700°C at 2000 bars. The data points of table 1 for 1000 and 2000 bars were included in the figures to indicate the quality of the fit.

ACKNOWLEDGMENTS

The author gratefully acknowledges Professor P. M. Orville for his advice during the course of this study.

REFERENCES

- Barnes, H. L., Helgeson, H. C., and Ellis, A. J., 1966, Ionization constants in aqueous solutions, in Clark, S. P., Jr., ed., *Handbook of physical constants*, revised ed.: Geol. Soc. America Mem. 97, p. 401-413.
- Benedict, Manson, 1939, Properties of saturated aqueous solutions of potassium chloride at temperatures above 250°C : *Jour. Geology*, v. 47, p. 252-276.
- Benrath, A., Gjedesbo, F., Schiffers, B. and Wunderlich, H., 1937, Solubility of salts and salt mixtures in water at temperatures above 100° : *Zeitschr. anorg. allgem. Chemie*, v. 231, p. 285-297.
- Buerger, M. J., Klein, G. E., and Donnay, Gabrielle, 1954, Determination of the crystal structure of nepheline: *Am. Mineralogist*, v. 39, p. 805-818.
- Copeland, C. S., Silverman, J., and Benson, S. W., 1952, The system $\text{NaCl-H}_2\text{O}$ at supercritical temperatures and pressures: *Jour. Chem. Physics*, v. 21, p. 12-16.
- Grover, J. E., and Orville, P. M., 1969, The partitioning of cations between coexisting single- and multi-site phases with application to the assemblages: orthopyroxene-clinopyroxene and orthopyroxene-olivine: *Geochim. et Cosmochim. Acta*, v. 33, p. 205-226.
- Hahn, T. W., and Buerger, M. J., 1955, The detailed structure of nepheline, $\text{KNa}_3\text{Al}_4\text{Si}_4\text{O}_{16}$: *Zeitschr. Kristallographie*, v. 106, p. 308-338.
- Helgeson, H. C., 1968, Geologic and thermodynamic characteristics of the Salton Sea geothermal system: *Am. Jour. Sci.*, v. 226, p. 129-166.
- Keevil, N. B., 1942, Vapor pressures of aqueous solutions at high temperatures: *Am. Chem. Soc. Jour.*, v. 64, p. 841-850.

- Kelley, K. K., 1935, Contributions to the Data on Theoretical Metallurgy—III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances: U.S. Bur. Mines Bull. 383, p. 132.
- Mayer, J. E. and Wintner, I. H., 1938, Measurements of Low Vapor Pressures of Alkali Halides: Jour. Chem. Physics, v. 6, p. 301-306.
- Roedder, E. W., 1958, Technique for the extraction and partial chemical analysis of fluid filled inclusions from minerals: Econ. Geology, v. 53, p. 235-269.
- Skinner, B. J., 1966, Thermal expansion, in Clark, S. P. Jr., ed., Handbook of physical constants, revised ed.: Geol. Soc. America Mem. 97, p. 75-96.
- Smith, J. V., and Tuttle, O. F., 1957, The nepheline-kalsilite system—I. X-ray data for the crystalline phases: Am. Jour. Sci., v. 255, p. 282-305.
- Sourirajan, S., and Kennedy, G. C., 1962, The system H₂O-NaCl at elevated temperatures and pressures: Am. Jour. Sci., v. 260, p. 115-141.
- Taylor, D., 1968, The thermal expansion of the sodalite group of minerals: Mineralog. Mag., v. 36, p. 761-769.
- Wellman, T. R., 1969, The vapor pressure of NaCl over decomposing sodalite: Geochim. et Cosmochim. Acta, v. 33, p. 1302-1303.
- , 1970, The stability of sodalite in a synthetic syenite plus aqueous chloride fluid system: Jour. Petrology, v. 11, p. 49-71.
- Wicks, C. E., and Block, F. E., 1963, Thermo-dynamic properties of 65 elements—their oxides, halides, carbides and nitrides: U.S. Bur. Mines Bull. 605, 146 p.
- Zimm, B. H., and Mayer, J. E., 1944, Vapor Pressures, Heats of Vaporization, and Entropies of some Alkali Halides: Jour. Chem. Physics, v. 12, p. 362-369.