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# Results from Boiling Temperature Measurements for Saturated Solutions in the Systems $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$ , $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ , and $\text{NaCl} +$ $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$

Joseph A. Rard

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**Results from Boiling Temperature Measurements for Saturated Solutions in the  
Systems NaCl + KNO<sub>3</sub> + H<sub>2</sub>O, NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O, and NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> +  
H<sub>2</sub>O**

Joseph A. Rard

Environmental Science Division, Energy and Environmental Directorate

University of California, Lawrence Livermore National Laboratory

Livermore, California 94550

**Abstract**

Boiling temperature measurements have been made for saturated ternary solutions of NaCl + KNO<sub>3</sub> + H<sub>2</sub>O and NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O over the full solute mole fraction range, along with the limiting binary solutions NaCl + H<sub>2</sub>O, NaNO<sub>3</sub> + H<sub>2</sub>O, and KNO<sub>3</sub> + H<sub>2</sub>O. Boiling temperatures have also been measured for the quaternary NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O mixtures with KNO<sub>3</sub>:NaNO<sub>3</sub> mole ratios of 1.01 and 1.19, which corresponding to the eutectic ratio and a near-eutectic ratio for the NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O subsystem. The maximum boiling temperature found for the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O system is 134 °C and for the NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O system is 160 °C, but boiling temperatures as high as 196 °C were measured the NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O system. These mixture compositions correspond to the major mineral assemblages that are predicted to control the deliquescence relative humidity of salts found by leaching dust samples from the proposed nuclear repository at Yucca Mountain, Nevada.

## 1. Introduction

The Yucca Mountain Project (YMP) Site in Nevada has been designated as a location for a permanent geological repository for the emplacement of high-level nuclear waste. Dust is expected to gradually deposit on the upper surface of the waste package. This dust will contain contributions both from local particulate material deposited during the construction of the repository and from dust brought in from ventilation that may contain contributions from atmospheric aerosols. Some of the salts found in this dust will deliquesce and could potentially initiate corrosion of the metallic alloy surface of the waste package surface. Whether or not this happens will depend mainly on the temperature, concentration, and chemical composition of the solutions formed when this deliquescence occurs, and whether the thus formed solution droplets are in direct contact with the surface of the waste package. The presence of the anions  $\text{Cl}^-$  and  $\text{NO}_3^-$ , and their relative and absolute concentrations, will have a major impact on the corrosive ability of these brines.

High concentrations of nitrate ion can occur in solutions formed by the evaporative concentration of groundwater whose initial nitrate concentration is low. This has been observed to occur from the evaporation of three types of ground waters found at the YMP site, and yields precipitates that include halite ( $\text{NaCl}$ ) and niter ( $\text{KNO}_3$ ) [Rosenberg, Gdowski, and Knauss, 2001; Alai, Sutton, and Carroll, 2004].

Thermodynamic modeling of the deliquescence behavior of the salts contained in the dust from the Yucca Mountain Repository Site indicates that mixtures of  $\text{NaCl}$  with  $\text{KNO}_3$  and / or  $\text{NaNO}_3$  will be the most prevalent mineral assemblies to occur [Wolery and Wang, 2004]. The presence of these nitrate salts will considerably reduce the relative humidity at which deliquescence will occur at high temperatures, as a result of their considerable solubility. For example, tabulated solubility data [Linke, 1965, page 263] imply the total

solution molality of the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  eutectic composition at  $150\text{ }^\circ\text{C}$  is  $\approx 95.5\text{ mol}\cdot\text{kg}^{-1}$  (90.0 mass-% solid) and is  $\approx 160\text{ mol}\cdot\text{kg}^{-1}$  (93.8 mass-% solid) at  $175\text{ }^\circ\text{C}$ .

Reverse deliquescence experiments have been reported for the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system at  $90\text{ }^\circ\text{C}$  [Craig, Carroll, and Wolery, 2004]. The measured deliquescence relative humidity (DRH) results agree well with predictions made using the EQ3/6 geochemical modeling code [Wolery and Jarek, 2003] for  $\text{NaNO}_3$  molality fractions  $x(\text{NaNO}_3) > 0.4$ , but there are significant discrepancies for solutions containing higher mole fractions of  $\text{KNO}_3$ . These  $x$  values are the salt molality fractions, that is,  $x(\text{NaNO}_3) = (\text{moles of NaNO}_3) / \{(\text{moles of NaNO}_3) + (\text{moles of KNO}_3)\}$ ; the amount of water is not included in the mole fraction calculations. However, the predicted molalities of the solutions in the vicinity of the eutectic at  $90\text{ }^\circ\text{C}$  are lower than the experimental values by about a factor of 2.

The origin of these significant errors in the model predictions arises from deficiencies in the Pitzer parameter [Pitzer, 1991] thermodynamic database used by the EQ3/6 geochemical modeling code [Wolery and Jarek, 2003]. Binary solution Pitzer parameters are available to around  $150\text{ }^\circ\text{C}$  for the  $\text{NaNO}_3(\text{aq})$  system [Rard and Wijesinghe, 2003], but the binary solution parameters for  $\text{KNO}_3(\text{aq})$  are only available at  $25\text{ }^\circ\text{C}$ , and the  $\theta(\text{Cl}, \text{NO}_3)$  mixing parameter required for modeling the thermodynamic properties of concentrated salt mixtures is similarly only available at  $25\text{ }^\circ\text{C}$ . The thermodynamic modeling calculations mentioned in the previous paragraph were based on the assumption that the  $\text{KNO}_3(\text{aq})$  and  $\theta(\text{Cl}, \text{NO}_3)$  Pitzer parameters do not vary with temperature, and their values were fixed at their known  $25\text{ }^\circ\text{C}$  values [Pitzer, 1991]. This approximation is expected to give increasingly more serious prediction errors as the temperature is increased because the saturated solution molalities increase rapidly with increasing temperature.

Because the temperature-dependent  $\text{KNO}_3(\text{aq})$  binary solution Pitzer parameters and  $\theta(\text{Na,K})$  parameter values needed for improving the thermodynamic modeling predictions are not likely to become available in the very near future, boiling temperature measurements were made for saturated solutions in the following systems:  $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$ ,  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ , and  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ . These measurements directly establish the upper temperatures at which deliquescence can occur in these salt mixtures, and will provide checks on the reliability of future geochemical modeling calculations.

## **2. Experimental Description**

All of the experimental measurements and data described in this report are detailed in YMP scientific notebook SN-LLNL-SCI-474-V4, pages 7 through 70.

### *2.1. The Boiling Temperature Apparatus and the Temperature Measurements*

The initial boiling temperatures for saturated solutions were measured in a high density PTFE (polytetrafluoroethylene) beaker into which was inserted a temperature probe and a stirrer to keep the solution mixed. A flat piece of PTFE was placed over the top of the beaker to reduce solvent evaporation, and the beaker was placed in a heating mantle that provided heating separately from the bottom and the sides of the beaker. Although this apparatus was satisfactory for determining the boiling temperatures of pure water and single salt systems, the heat and water losses were too large, and the thermal conductivity of the PTFE was too low, to allow the boiling temperatures of the mixed salt solutions to be determined. The first apparatus was replaced by a glass apparatus for all of the remaining measurements.

The second boiling temperature apparatus was made from a flat bottom flask to which an upper glass section was clamped firmly in place. The upper section had four standard

taper openings on the top. The largest (central) opening was fitted with a water-cooled condenser column to reduce loss of water during the experiments. The shaft of a three-blade propeller stirrer was inserted in the solution through the center of the condenser column, which allowed the solution to be rapidly mixed to reduce the formation of concentration and temperature gradients. The other three ports were located at 120° intervals towards the edge of the top of the upper section. All three of these outer ports were closed with rubber stoppers during the boiling temperature measurements. One port was opened when dry salts (using a plastic funnel) or water were added to this vessel, and for the visual observation of the boiling of the solution, but it was sealed with the rubber stopper at other times. The other two ports were used for thermocouple probes, which were inserted through the center of the rubber stoppers. The internal volume of the boiling temperature apparatus was approximately one liter, of which about 125 to 150 mL was occupied by solution and solid during the boiling temperature experiments. The bottom section of the apparatus was inserted into a heating mantle, with heat being applied separately to the bottom and to the sides of the apparatus. The temperature of the heating mantle was always kept above the boiling temperature of the solution during the measurements.

Several series of experiments with the glass boiling temperature apparatus involved the use of an AG4554 Microprecision thermocouple interfaced with a Beamex Multifunctional Calibrator # 009215, which shall be designated as probe “A”. Temperatures measured with the probe “A” system could be read to 0.01 °C. This thermocouple probe was inserted through the rubber stopper into the solution near the edge of the flask outside the sweep of the propellers of the stirrer. However, the boiling temperature determined for pure water with this probe, 101.12 °C, was approximately 1.5 °C higher than expected from literature data [Weast, 1987–1988] for the experimental pressure conditions. This suggested that the

temperatures measured with probe “A” were slightly higher than the correct boiling temperatures, presumably because the probe were located near the edges of the apparatus where heat was being applied and there was a slight time lag while the added heat was being dispersed throughout the solution.

A second thermocouple probe was added for subsequent experiments. The second temperature measurement system consists of an  $\Omega$ EOMEGA 450ATT Thermocouple Type T (ID number GG353) interfaced with an  $\Omega$ EOMEGA calibrator number TC00047-04, which we refer to as System “B”. This thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. Temperatures measured with the probe “B” system could only be read to the nearest 0.1 °C with the probe “B” system.

A large number of temperature measurements were made using both probes from ambient temperature to almost 200 °C, which are summarized in Table 1. The difference in temperatures recorded between the two probes are insignificant at room temperature, but are about  $\Delta T \approx 1$  °C at 100 °C, and are about  $\Delta T \approx 2$  °C at 200 °C. The inner probe always gave lower temperature readings, and gave values more closely corresponding to the correct boiling temperature of pure water, see Table 2. Increasing the stirring rate had little effect on the differences recorded between the two temperature probes. Both temperature probes were in calibration, and their calibration uncertainties are ca. 0.1 to 0.3 °C. Thus the temperature differences between the two probes above 100 °C exceed the calibration uncertainties. This implies that the slightly high nominal temperature readings obtained with probe “A” result from heat transport limitations in our boiling temperature apparatus. Accordingly, all of the temperatures recorded with probe “A” were adjusted for these

temperature differences. These corrections for probe “A” bring the temperatures measured with the two probes into good agreement.

Three determinations were made of the boiling temperature of water, and the results are listed in Table 2. The average of these three boiling temperatures after adjusting the temperature readings of probe “A” to agree with probe “B”, is  $100.5 \pm 0.1$  °C. The atmospheric pressure when these three boiling temperatures were measured ranged from 0.9920 bar to 0.9941 bar or  $(9920/1.01325) = 0.9790$  atm to  $(0.9941/1.01325) = 0.9811$  atm. Examination of the critically assessed vapor pressures of water in the Handbook of Chemistry and Physics [Weast, 1987–1988] indicates that the correct boiling temperature for water at the average of these three pressures should be 99.4 °C. This temperature difference implies that there is a small effect from heat transport limitations even near the center of our boiling temperature apparatus. Accordingly, the nominal temperatures were adjusted downward by an additional 1.1 °C to yield complete agreement for the boiling temperature of water with the probe “B” system. The boiling temperatures for the saturated binary salt solutions NaCl + H<sub>2</sub>O, NaNO<sub>3</sub> + H<sub>2</sub>O, and KNO<sub>3</sub> + H<sub>2</sub>O, Table 2, after making the appropriate corrections to the readings, are in good agreement with literature data. These comparisons are described later in the *Section 3.1. Boiling Temperatures for the Single Salt Systems NaCl + H<sub>2</sub>O, NaNO<sub>3</sub> + H<sub>2</sub>O, and KNO<sub>3</sub> + H<sub>2</sub>O.*

The total corrections for our recorded (nominal) temperatures for both of thermocouple probe systems are summarized in Table 3. The corrections for probe “B” are constant  $-1.1$  °C, but for probe “A” range from  $-1.1$  °C to  $-3.25$  °C. Tables 4, 5, and 6 contain the boiling temperatures for the mixed salt systems. Both the nominal and corrected temperatures are reported. The corrected temperatures are recommended. Based on the size of the temperature corrections, and the reproducibility of the boiling temperatures measured for

pure H<sub>2</sub>O and saturated aqueous solutions of the single salts (Table 2), the uncertainties in the reported corrected temperatures are estimated to be about 0.5 °C for temperatures around 100 °C and are about 1 °C for temperatures around 200 °C.

To check whether super heating was occurring, the boiling temperature of the saturated NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O maximum boiling eutectic was determined in the usual method. Teflon boiling chips were then added to the solution in the apparatus to provide additional sites for bubble formation and the boiling temperature was redetermined. Finally, glass beads were added to the solution and the boiling temperature apparatus and the boiling temperature was determined again. All three boiling temperatures agreed to within 0.9 °C which indicates that superheating of the solution was not significant. These boiling temperatures are documented in Table 5.

No calibrated pressure measuring system was available for these experiments, so the reported pressure for each experiment is the official pressures at LLNL at the time of the boiling temperature measurement, as given on the LLNL internet weather web site.

## *2.2. Source Chemicals, Preparation of the Solutions, and the Chemical Stability of the Solutions*

The mixtures used for the boiling temperature experiments were prepared by weight using the dry salts and purified water. The source NaNO<sub>3</sub> and KNO<sub>3</sub> chemicals used for all of the experiments were supplied by J. T. Baker, as was the NaCl used for the last NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O boiling temperature experiment, with lot analysis results provided by the supplier. All of the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O experiments and the majority of the NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O experiments involved the use of G. Frederick Smith (GFS) NaCl. The salt samples were weighed to a precision of  $1 \times 10^{-4}$  g using an in calibration Satorius balance (SN80110582), with daily checks on the accuracy using standard weights, and were

thus “Q” level measurements. Based on the weighing uncertainties and calibrations, all sample weights should be reliable to  $\leq 0.01$  %. All water used in the boiling temperature experiments was purified using a Barnstead E-Pure water treatment system.

No attempt was made to dry the chemicals used for the experiments. The purities of the GFS NaCl and the J. T. Baker KNO<sub>3</sub> were given by the supplier as 99.9 %. Based on the cation and anion impurity analysis results reported by the supplier, other anions and cations that were present were in insignificant amounts, and is likely that most of the 0.1 % impurities are actually residual water. Dehydration experiments for two commercial samples of NaCl(s) [Rard, 1996, Table 2] showed the presence of 0.1– 0.15 mass-% residual water in the original samples, which is not completely removed until the NaCl samples are heated to  $\approx 500$  °C. The purity of the J. T. Baker NaCl was given by the supplier as 100.2 % and for the KNO<sub>3</sub> as 100.3 %. Obviously, the actual purity can not exceed 100 %, and the slightly larger values are due to the uncertainty in their chemical analysis. Again, for this NaCl the only significant impurity is likely to be residual water. The effect of the presence of the residual water will largely cancel out when solute mole fractions are calculated.

The number of moles of each salt were calculated from the sample weights assuming that the molar masses are 58.443 g·mol<sup>-1</sup> for NaCl, 84.99 g·mol<sup>-1</sup> for NaNO<sub>3</sub>, and 101.11 g·mol<sup>-1</sup> for KNO<sub>3</sub>. In principle, the calculation of the number of moles should be based on sample masses rather than the weights. That is, buoyancy corrections are needed. However, the densities of NaCl, NaNO<sub>3</sub>, and KNO<sub>3</sub> are nearly the same: 2.165 g·cm<sup>-3</sup>, 2.261 g·cm<sup>-3</sup>, and 2.109 g·cm<sup>-3</sup>, respectively [Weast, 1987–1988]. Consequently, the buoyancy corrections need not be made because their effects will almost completely cancel when solute mole fractions are calculated.

Based on the uncertainties and weighing errors described in the preceding three paragraphs, the solute mole fractions reported in this paper should be accurate to  $\leq 0.2\%$ .

During the boiling temperature measurements, the  $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$ ,  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ , and  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  solutions were heated for extended periods of time. There was no direct evidence that any decomposition of the electrolytes had occurred, or for the occurrence of any chemical reaction between the chloride and nitrate ions. That is, no color changes occurred in the solution, nor were the odors of chlorine or nitrogen oxides detected. However, to check this conclusion, samples of the liquid phase at the maximum boiling temperature of the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  eutectic and from the last  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  experiment were removed in order to be analyzed for nitrite ion,  $\text{NO}_2^-$ , which is a species that could potentially form if any the nitrate ions are being reduced by chloride at the high temperatures. These liquid samples became completely solid after they cooled by just a few degrees. Samples of the source chemicals  $\text{NaCl(s)}$ ,  $\text{NaNO}_3(\text{s})$ , and  $\text{KNO}_3(\text{s})$  were also analyzed to determine whether any detectible amounts nitrite ions were initially present.

Approximately 0.5 g samples of each solid to be analyzed were dissolved in 50 mL of purified water, and they were then analyzed for  $\text{NO}_2^-$ , using ion chromatography, by Maureen Alai (documented in SN-LLNL-SCI no. 478-V2). The presence of  $\text{NO}_2^-$  was not detected in any of the analyzed samples, with a detection limit of about 1 ppm in the absence of chloride. However, the analysis for  $\text{NO}_2^-$  in the  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  solution was much less sensitive, because the intense chloride peak overlaps with and would mask a weak peak for  $\text{NO}_2^-$ .

A sample of the residue from the last experiment of the first series of experiments for the  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  high boiling temperature solutions, with  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\} \approx 1.01$ , was dissolved in water at room temperature. A rough pH determination for this solution was made using ColorpHast pH indicator strips. The observed  $\text{pH} \approx 6$  is equal to that expected for a  $\text{CO}_2$  saturated aqueous solution. Because the solution pH was slightly acidic, it was concluded that the prolonged heating of the saturated  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  solution at  $\approx 180^\circ\text{C}$  did not result in the formation of basic species (such as  $\text{NaOH}$  and  $\text{KOH}$ ), and therefore no significant amounts of  $\text{HCl}$  or  $\text{HNO}_3$  were lost from the prolonged heating of the solutions.

Based on the observations described in the three preceding paragraphs, we conclude that prolonged heating of the concentrated mixed electrolyte solutions did not cause any detectible amount of sample decomposition or other chemical changes. Thus the measured boiling temperatures pertain to solutions having the relative salt compositions listed in the tables.

### *2.3. Basic Procedure for the Determination of Boiling Temperatures of Saturated Solutions*

The basic experimental procedure is as follows. Approximately 100 to 150 mL of purified water (the exact amount is not important) was added to the boiling temperature apparatus and the heaters in the heating mantle were turned on to begin the heating process. A sample of one of the salts was weighed in a plastic weighing boat, and the weighed solid was transferred to the boiling temperature apparatus through an open port. This addition of salt was repeated until sufficient salt was present in the apparatus to yield a saturated solution together with an excess of solid phase. Heating was continued until the solution began boiling, and the boiling temperature of the saturated solution was recorded. A sample of a second salt was then weighed and transferred to the boiling temperature apparatus to

produce a mixed salt system containing excess solid salt, and the boiling temperature of this mixture was determined in the same manner. Generally, additional amounts of the second salt were added in stages, and the saturated solution boiling temperatures were measured for these additional mixture compositions. The boiling temperatures of the saturated solutions in the mixed salt systems were always significantly higher than those of the corresponding single salt systems, and sometimes this temperature increase was sufficient to cause all of the solid salts that had been added to dissolve. When this happened, an additional amount of the first salt was added to yield another saturated solution. At the end of the working day, the heaters were turned off and the solution in the apparatus was allowed to cool to ambient temperature, which resulted in the sample becoming completely or mostly solid.

The solid mixture resulting from these experiments was sometimes used as the starting mixture for additional experiments on the following or a subsequent day. When this was to be done, the solid residue from the earlier experiment was reheated, generally with the addition of some purified water, until most of the residue has redissolved and the solution was boiling. The measured boiling temperature for this reheated mixture was generally slightly higher than the earlier determination using the freshly prepared mixture. This boiling temperature differences resulted from the formation of solid solutions when the samples were allowed to cool to room temperature, and this phenomenon is discussed later in the section *Boiling Temperatures for the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  System*.

### **3. Experimental Results and Discussion**

#### *3.1. Boiling Temperatures for the Single Salt Systems $\text{NaCl} + \text{H}_2\text{O}$ , $\text{NaNO}_3 + \text{H}_2\text{O}$ , and $\text{KNO}_3 + \text{H}_2\text{O}$*

The corrected boiling temperatures for saturated solutions of the single salts in water are given in the last column of Table 2. The average value for the boiling temperature of NaCl + H<sub>2</sub>O with NaCl(s) as the solid phase obtained from three separate measurements is  $107.7 \pm 0.1$  °C, where the measure of precision given in this report is one standard deviation. Five separate determinations for the boiling temperature of NaNO<sub>3</sub> + H<sub>2</sub>O with NaNO<sub>3</sub>(s) as the solid phase yield an average value of  $119.6 \pm 0.3$  °C, and five boiling temperature determinations for KNO<sub>3</sub> + H<sub>2</sub>O with KNO<sub>3</sub>(s) as the solid phase yield an average value of  $114.6 \pm 0.5$  °C. The atmospheric pressure ranged from 0.989 to 0.996 bar during these boiling temperature experiments, which corresponds to vapor pressures between  $(0.989/1.01325) = 0.976$  and  $(0.996/1.01325) = 0.983$  atm. The “normal boiling point” of a solution is defined as the temperature at which the solvent (in this case, water) has a vapor pressure of exactly one atmosphere.

Timmermans [Timmermans, 1960; pages 306, 307, 387, 388, 554, and 555] lists values of the “normal boiling points” of saturated aqueous solutions of these salts, mainly from measurements made in the 1880s and early 1900s when the temperature scales were not as well defined. Boiling temperatures listed by Timmermans for saturated NaCl + H<sub>2</sub>O solutions are 108.50, 108.668, and 109 °C; for NaNO<sub>3</sub> + H<sub>2</sub>O are 120.20, 121, and 122 °C; and are 115.549, 115.9, and 118 °C for KNO<sub>3</sub> + H<sub>2</sub>O. The last value for KNO<sub>3</sub> + H<sub>2</sub>O is presumably an outlier. Taking into account the pressure difference between 1 atm and our experimental conditions of 0.976 to 0.983 atm, the literature boiling temperatures at 1 atm should be lowered by about 1 °C to make them comparable to our  $\approx 0.98$  atm pressure condition, which brings them into good agreement with the present measurements.

Although these pressures should be accurate, they are the ambient outdoor pressures and will differ slightly from the pressure inside the laboratory building where the boiling temperature experiments were performed.

### *3.2. Boiling Temperatures for the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O System*

The corrected boiling temperatures for saturated solutions in the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O system are reported in Table 4 as a function of the composition fractions  $x(\text{NaCl})$  and  $x(\text{KNO}_3)$ , and are plotted in Figure 1. These composition fractions are nominal values based on the amount of each solid salt added to the solution. Obviously, when NaCl precipitates as the solid phase, the composition of the solution phase will have a slightly different and lower composition fraction  $x(\text{NaCl, solution})$  than the nominal value, where  $x(\text{NaCl, solution}) < x(\text{NaCl})$ . Similarly, when the solid phase is KNO<sub>3</sub>, then  $x(\text{KNO}_3, \text{solution}) < x(\text{KNO}_3)$ . However, at the observed eutectic composition  $x(\text{NaCl}) \approx 0.32$  and  $x(\text{KNO}_3) \approx 0.68$ , which corresponds to the maximum boiling temperature, the solution composition fractions should be the same as their nominal values. Also given in Table 4 are the boiling temperatures for the limiting cases of the single salt constituents NaCl + H<sub>2</sub>O and KNO<sub>3</sub> + H<sub>2</sub>O, which correspond to  $x(\text{NaCl}) = 1$  and  $x(\text{KNO}_3) = 1$ , respectively. The boiling temperatures for the saturated NaCl + H<sub>2</sub>O and KNO<sub>3</sub> + H<sub>2</sub>O solutions reported in this table are the averages of the replicate determinations reported in Table 2.

Four solid phases can be formed by combining the Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> ions: NaCl, KCl, KNO<sub>3</sub>, and NaNO<sub>3</sub>. However, available solubilities [Linke, 1965, page 265] for the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O system at 20, 30, 40, and 91 °C give evidence that the only stable solid phases that form in contact with these saturated solutions are NaCl and KNO<sub>3</sub>, along with both salts being present at the eutectic composition. Although there are no abrupt variations in the boiling temperatures with the mole fraction compositions that would indicate the

presence of an additional solid phase such as KCl being present in our saturated solutions, addition compositions would need to be studied with  $x(\text{NaCl}) > 0.5$  to verify the presence or absence of KCl. Our boiling temperatures are consistent with the eutectic composition occurring at  $x(\text{NaCl}) \approx 0.32$ ,  $x(\text{KNO}_3) \approx 0.68$ , and a maximum boiling temperature of 133.8 °C. For solutions with compositions  $x(\text{NaCl}) > 0.32$ , the solid phase should be NaCl, for solutions with  $x(\text{NaCl}) < 0.32$  the solid phase should be  $\text{KNO}_3$ , whereas at the eutectic composition both solid phases will be present.

### 3.3. Boiling Temperatures for the $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ System

The corrected boiling temperatures for saturated solutions in the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system are reported in Table 5 as a function of the composition fractions  $x(\text{NaNO}_3)$  and  $x(\text{KNO}_3)$ , and are plotted in Figure 2. These composition fractions are nominal values based on the amount of each solid salt added to the solution. Also given are the boiling temperatures for the limiting cases of the single salt constituents  $\text{NaNO}_3 + \text{H}_2\text{O}$  and  $\text{KNO}_3 + \text{H}_2\text{O}$ , which correspond to  $x(\text{NaNO}_3) = 1$  and  $x(\text{KNO}_3) = 1$ , respectively. The boiling temperatures for  $\text{NaNO}_3 + \text{H}_2\text{O}$  and  $\text{KNO}_3 + \text{H}_2\text{O}$  in this table are the averages of the replicate determinations reported in Table 2.

The possible solid phases in the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system are  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and their solid solutions. A maximum is observed in the boiling temperatures around 160 °C with at composition fraction of  $x(\text{NaNO}_3) \approx 0.46$  and  $x(\text{KNO}_3) \approx 0.54$ , which should correspond to the eutectic composition. See Figure 2 and Table 5. This maximum boiling temperature is  $\approx 40$  °C above that observed for the limiting binary solution  $\text{NaNO}_3 + \text{H}_2\text{O}$  and  $\approx 52$  °C above that observed for the other limiting binary solution  $\text{KNO}_3 + \text{H}_2\text{O}$ . Available solubilities [Linke, 1965; page 263] for the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system yield eutectic compositions of  $x(\text{NaNO}_3) = 0.391$  at 125 °C,  $x(\text{NaNO}_3) = 0.425$  at 150 °C, and  $x(\text{NaNO}_3)$

= 0.467 at 175 °C, which are consistent with our result at the maximum boiling temperature of  $\approx 160$  °C. The solubility data tabulated by Linke yield total molalities  $m_T$  (which is equal to the ionic strength because both electrolytes have the same charge type) for  $\text{NaNO}_3 + \text{KNO}_3$  of  $m_T = 70.6 \text{ mol}\cdot\text{kg}^{-1}$  at 125 °C,  $m_T = 95.5 \text{ mol}\cdot\text{kg}^{-1}$  at 150 °C, and  $m_T = 160 \text{ mol}\cdot\text{kg}^{-1}$  at 175 °C. Graphical interpolation of these results yields an estimate of the molality / ionic strength of the eutectic composition  $m_T \approx 105 \text{ mol}\cdot\text{kg}^{-1}$  at the maximum boiling temperature of  $\approx 160$  °C. These saturated solution molalities are very much higher than those that are observed for the single salt systems  $\text{NaNO}_3 + \text{H}_2\text{O}$  and  $\text{KNO}_3 + \text{H}_2\text{O}$  at these temperatures [Linke, 1965; pages 263, 1069, and 1070].

Some of the boiling temperature experiments reported in Table 5 involved separate boiling temperature measurements using the same mixtures of  $\text{NaNO}_3 + \text{KNO}_3$ , but which were made on separate days. The first boiling temperature determined for each of these compositions was measured after the fresh addition of one or more of the component salts. After these initial determinations were made, the heater was turned off after normal working hours, which permitted the solutions to cool down. After cooling to room temperature, little or no liquid phase remained and the samples were mostly or entirely solid. The solid residue was reheated with addition of small amounts of water to produce the solution used for the second boiling temperature determination. In the second boiling temperature determinations, the solid phase consisting of some of the undissolved residue remaining from the previous experiment.

When these very concentrated hot solutions are allowed to cool by just a few degrees, large amounts of solid are formed owing the rapid variation of the saturation molalities with temperature. The resulting solid phase is white, glassy in appearance, very hard, and somewhat slow to dissolve. According to the information provided by Linke [Linke, 1965;

pages 261 and 262], below 105 °C both solid NaNO<sub>3</sub> and KNO<sub>3</sub> are stable as pure phases in contact with saturated NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O solutions, depending on the salt ratio, but above 150 °C they form a continuous series of solid solutions. The observed higher boiling temperatures for the second determinations refer to the glassy-like solid solution, and the solution phase should presumably have a composition close to or identical to the NaNO<sub>3</sub> + KNO<sub>3</sub> solid solution present during that experiment. These second determinations presumably represent boiling temperature measurements for saturated solutions in contact with the thermodynamically stable solid phase. The lower boiling temperatures for the first determination apparently refer to a metastable solid solution that differs in mole fraction composition from the solution phase.

Comparing the boiling temperature differences observed for the initial measurement at a fixed salt ratio (with a solid phase having a solute ratio different from the solution solute ratio) and the second measurement (with the solid phase being a solid solution presumably having the same solute ratio as the solution), Table 5, indicates that the boiling temperatures that were measured following the addition of one of the solutes may be low by  $\Delta T \approx 1$  °C at 123 °C, by  $\Delta T \approx 2$  °C at 134 °C, by  $\Delta T \approx 6$  °C at 155 to 160 °C, compared to the “correct” boiling temperatures for the equilibrium solid solution compositions.

#### *3.4. Boiling Temperatures for the NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O System*

The corrected boiling temperatures for saturated solutions in the NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O system are reported in Table 6 as a function of the composition fractions  $x(\text{NaCl})$ ,  $x(\text{NaNO}_3)$ , and  $x(\text{KNO}_3)$ , and are plotted in Figure 3. These composition fractions are nominal values based on the amount of each solid salt added to the solution. Also given are the boiling temperatures for the limiting two salt system without NaCl, NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O, which correspond to  $x(\text{NaCl}) = 0$ . Three separate series of experiments were

performed. One series of experiments was made with  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\} \approx 1.01$  and with variable amounts of NaCl, and two series were made with  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\} \approx 1.19$  and with variable amounts of NaCl. These two values of  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\}$  were chosen to correspond to  $x(\text{NaNO}_3) \approx 0.50$  and  $x(\text{NaNO}_3) \approx 0.46$  for the limiting two salt mixture  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ . These two ratios correspond to the potassium/sodium ratios occurring at and near the maximum boiling temperature eutectic composition in the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system.

Addition of NaCl resulted in a large increase in the observed boiling temperatures, with the highest observed boiling temperature being 195.7 °C. Because the observed boiling temperatures continued to increase with increasing values of  $x(\text{NaCl})$ , both when  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\} \approx 1.01$  and when  $\{\text{moles}(\text{KNO}_3)/\text{moles}(\text{NaNO}_3)\} \approx 1.19$ , it is likely that adding more NaCl to further increase the values of  $x(\text{NaCl})$  will result in higher boiling temperatures for the  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system that may significantly exceed 200 °C at the eutectic composition.

The boiling temperatures determined for  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  solutions that formed after redissolving most of the glassy-like solid solutions from a previous experiment were always higher than boiling temperature obtained right after addition of one of the salts. The cause of this difference should be the same as described for the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  mixtures. That is, the initial (lower) boiling temperature refers to a saturated solution in contact with a solid phase having a solute ratio different from the solution solute ratio, whereas the redetermined boiling temperature refers to the solid phase being a solid solution presumably having the same solute ratio as the solution phase.

*3.5. A Comparison of Predicted and Measured Boiling Temperatures for the  $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$  and  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  Eutectic Compositions*

Wolery [Wolery, 2004] has used the EQ3/6 Software and its associated Pitzer parameter database [Wolery and Jarek, 2003] to predict that the maximum boiling temperature for the  $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$  system will be  $130\text{ }^\circ\text{C}$ , and that for the  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  system will be  $140\text{ }^\circ\text{C}$ , both at pressures  $\approx 0.98\text{ bar}$ . The predicted boiling temperature of  $130\text{ }^\circ\text{C}$  for the  $\text{NaCl} + \text{KNO}_3 + \text{H}_2\text{O}$  ternary system agrees well with our experimental boiling temperature of  $133.8\text{ }^\circ\text{C}$  at the slightly higher pressure of  $\approx 0.99\text{ bar}$ . However, for the  $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  quaternary system the predicted maximum boiling temperature is low by nearly  $60\text{ }^\circ\text{C}$ . This significant prediction error is a result of the unavailability of temperature dependent Pitzer parameters for the  $\text{KNO}_3 + \text{H}_2\text{O}$  binary system and the  $\theta(\text{Cl},\text{NO}_3)$  mixing parameter, as described in the Introduction.

### *3.6. A Brief Qualitative Thermodynamic Analysis of the High Boiling Temperatures Observed for the $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ and $\text{NaCl} + \text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$ Mixtures*

Solubilities of salts are generally significantly higher when the equilibrium solid melts at lower temperatures, compared to the solubilities of solid salts that melt at higher temperatures. Anhydrous  $\text{NaNO}_3(\text{s})$  melts at  $307\text{ }^\circ\text{C}$  and anhydrous  $\text{KNO}_3(\text{s})$  melts at  $335\text{ }^\circ\text{C}$ , which are much higher than the boiling temperatures of the saturated solutions ( $119.6$  and  $114.5\text{ }^\circ\text{C}$ , respectively) determined in this study. However the low melting eutectic in the anhydrous  $\text{NaNO}_3 + \text{KNO}_3$  system occurs at a much lower temperature of  $221\text{ }^\circ\text{C}$  [Simonson, 2004], which is only about  $60\text{ }^\circ\text{C}$  above the maximum boiling temperature measured for the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  eutectic composition reported in Table 5. The observed much higher solubilities of aqueous  $\text{NaNO}_3 + \text{KNO}_3$  mixtures compared to the single salt systems is mainly a consequence of the much lower melting temperature that occurs for the solid solutions that become the thermodynamically stable phase in contact with the saturated aqueous mixtures at higher temperatures. Both  $\text{NaNO}_3$  and  $\text{KNO}_3$  are

associated electrolytes, whereas NaCl is much less associated and therefore is hydrated more strongly by water. As a consequence, adding NaCl to the  $\text{NaNO}_3 + \text{KNO}_3 + \text{H}_2\text{O}$  causes a significant decrease in the vapor pressure of water and the resulting large increase in the observed boiling temperature of these mixtures, compared to nitrate salt mixtures [Simonson, 2004].

The reason for the substantial increase in solubility at the maximum boiling eutectic composition can be understood from the following thermodynamic analysis. For simplicity, the analysis will be restricted to the solubility of a single salt in water, but the same basic analysis will apply to mixed salts.

Consider the dissolution of an unhydrated solid salt in water to form its saturated solution:



The change in the Gibbs free energy for this reaction is then given by the equation

$$\Delta_f G_m^\circ(\text{MX, s}, T) + \Delta_{\text{sol}} G_m^\circ(\text{MX, aq, sat}, T) = \Delta_f G_m^\circ(\text{M}^+, \text{aq}, T) + \Delta_f G_m^\circ(\text{X}^-, \text{aq}, T) \quad (2)$$

where  $\Delta_f G_m^\circ(\text{MX, s}, T)$ ,  $\Delta_f G_m^\circ(\text{M}^+, \text{aq}, T)$ , and  $\Delta_f G_m^\circ(\text{X}^-, \text{aq}, T)$  are the standard Gibbs free energies of formation of  $\text{MX(s)}$ ,  $\text{M}^+(\text{aq})$ , and  $\text{X}^-(\text{aq})$ , respectively, at the indicated absolute temperature  $T$  in kelvins. The standard Gibbs free energy of solution at the temperature  $T$  is related to the molality of the saturated solution  $m(\text{sat})$  by

$$\begin{aligned}\Delta_{\text{sol}}G_{\text{m}}^{\circ}(\text{MX}, \text{aq}, \text{sat}, T) &= -RT\ln\{m(\text{sat})^2\gamma_{\pm}(\text{sat})^2\} \\ &= -RT\ln K_{\text{s}}\end{aligned}\quad (3)$$

where  $\gamma_{\pm}(\text{sat})$  is the mean molal activity coefficient of the electrolyte in the saturated solution,  $K_{\text{s}} = m(\text{sat})^2\gamma_{\pm}(\text{sat})^2$  is the standard thermodynamic solubility product, and  $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is the universal gas constant. Combining equations (2) and (3) and rearranging them yields the following relation for  $K_{\text{s}}$ :

$$K_{\text{s}} = \exp\left[\frac{\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{MX}, \text{s}, T) - \Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{M}^{+}, \text{aq}, T) - \Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{X}^{-}, \text{aq}, T)}{RT}\right] \quad (4)$$

Values of the standard Gibbs energies of formation of thermodynamically stable ions and compounds are negative, and the numerical value of the temperature-dependent difference function  $[\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{MX}, \text{s}, T) - \Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{M}^{+}, \text{aq}, T) - \Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{X}^{-}, \text{aq}, T)]$  will determine the value of  $K_{\text{s}}$  at each temperature  $T$ . As the temperature increases, the numerical value of this function shifts in the positive direction for solutes with prograde solubilities (i.e., solutes whose solubilities increase with temperature) and the values of  $K_{\text{s}}$  become larger. However, at high temperatures, values of  $\gamma_{\pm}$  at any particular molality generally decrease significantly with increasing temperature, so  $m(\text{sat}) = \{K_{\text{s}}/\gamma_{\pm}(\text{sat})^2\}^{1/2}$  increases rapidly with temperature. The prediction of  $m(\text{sat})$  also requires a knowledge of the activity coefficients.

For a comparable thermodynamic analysis of the solubilities of mixed salt systems where the thermodynamically stable solid phase is a solid solution, the variation of  $\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{MX}, \text{s}, T)$

with the mole fraction of component MX in the solid solution needs to be taken into consideration. However, this analysis is beyond the scope of the present report.

## **Conclusions**

Boiling temperatures have been measured for the NaCl + KNO<sub>3</sub> + H<sub>2</sub>O, NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O, and NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O systems. The observed boiling temperatures for the latter system are considerably higher than values predicted from geochemical modeling calculation using EQ3/6 as a result of limitations of the thermodynamic database. The experimental results indicate that the NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O mineral assemblage occurring in some dust samples from the Yucca Mountain Site will deliquesce at temperatures  $\geq 196$  °C.

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**Table 1. Comparison of Temperatures Measured with the Two Thermocouple Measuring Systems.<sup>a</sup>**

temperature/°C probe “A”	temperature/°C probe “B”	temperature difference/°C (probe “A” – probe “B”)
22.85	22.8	0.0 <sub>5</sub>
23.02	22.9	0.1 <sub>2</sub>
25.24	25.2	0.0 <sub>4</sub>
58.20	58.0	0.2 <sub>0</sub>
101.14	100.5	0.6 <sub>4</sub>
101.13	100.4	0.7 <sub>3</sub>
101.35	100.6	0.7 <sub>5</sub>
116.73	115.9	0.8 <sub>3</sub>
118.53	117.6	0.9 <sub>3</sub>
121.44	120.3	1.1 <sub>4</sub>
121.94	120.9	1.0 <sub>4</sub>
121.95	120.9	1.0 <sub>5</sub>
124.7	123.6	1.1
125.75	124.4	1.3 <sub>5</sub>
129.53	128.0	1.5 <sub>3</sub>
133.45	131.8	1.6 <sub>5</sub>
138.7	136.9	1.8
146.2	144.7	1.5
155.2	153.8	1.4
156.92	155.4	1.5 <sub>2</sub>
161.21	160.0	1.2 <sub>1</sub>
161.46	160.3	1.1 <sub>6</sub>
162.40	161.0	1.4 <sub>0</sub>
162.4	160.7	1.7
163.3	161.5	1.8
176.05	174.5	1.5 <sub>5</sub>

178.8	177.3	1.5
184.60	182.3 <sub>5</sub>	2.2 <sub>5</sub>
191.2	190.7	1.5
192.22	189.90	2.3 <sub>2</sub>
198.71	196.8 <sub>5</sub> (Probe "C")	1.8 <sub>6</sub>

<sup>a</sup> System "A" consists of an AG4554 Microprecision thermocouple interfaced with a Beamex Multifunctional Calibrator # 009215. This thermocouple probe was inserted into the solution near the edge of the flask outside the sweep of the propellers of the stirrer. System "B" consists of an ΩEOMEGA 450ATT Thermocouple Type T (ID number GG353) interfaced with an ΩEOMEGA calibrator number TC00047-04. This thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. Probe "C" contained the same thermocouple as system "B" but had a different calibrator, ΩEOMEGA CL8500, Bectel ID 009428. The temperatures measured with "probe "A" were recorded to 0.01 °C if the variations during the measurements were small, and to the nearest 0.1 °C if they were larger. However, those temperatures measured with probe "B" could only be recorded to the nearest 0.1 °C. When the recorded temperatures with the two probes differ in precision, the last figure for the temperature difference is subscripted.

**Table 2. Boiling Temperatures for Pure H<sub>2</sub>O, and Saturated Aqueous Solutions of a single Salt in H<sub>2</sub>O.<sup>a</sup>**

System	pressure (bar)	probe "A" (°C)	probe "B" (°C)	temperature/°C corrected
H <sub>2</sub> O(l)	0.9943	101.12		99.4
H <sub>2</sub> O(l)	0.9920	101.35	100.6	99.5 <sub>5</sub>
H <sub>2</sub> O(l)	0.9941	101.14	100.5	99.4
H <sub>2</sub> O(l)	0.9941	101.13	100.4	99.3
NaCl + H <sub>2</sub> O	0.9956	109.63		107.7
NaCl + H <sub>2</sub> O	0.9956	109.70		107.8
NaCl + H <sub>2</sub> O	0.9895	109.46		107.6
NaNO <sub>3</sub> + H <sub>2</sub> O	0.9924	121.18		119.2
NaNO <sub>3</sub> + H <sub>2</sub> O	0.9946	121.42		119.4
NaNO <sub>3</sub> + H <sub>2</sub> O	0.9949	121.60		119.6
NaNO <sub>3</sub> + H <sub>2</sub> O	0.9941	121.94	120.9	119.9
NaNO <sub>3</sub> + H <sub>2</sub> O	0.9965	121.95	120.9	119.9
KNO <sub>3</sub> + H <sub>2</sub> O	0.9916	115.9		114.0
KNO <sub>3</sub> + H <sub>2</sub> O	0.9995	115.87		113.9
KNO <sub>3</sub> + H <sub>2</sub> O	0.9891	116.4		114.5
KNO <sub>3</sub> + H <sub>2</sub> O	0.9936	117.2		115.3
KNO <sub>3</sub> + H <sub>2</sub> O	0.9918	116.73	115.9	114.8

<sup>a</sup> Probe "A" consists of an AG4554 Microprecision thermocouple interfaced with a Beamex Multifunctional Calibrator # 009215. This thermocouple probe was inserted into the solution near the edge of the flask outside the sweep of the propellers of the stirrer. Probe "B" consists of an ΩEOMEGA 450ATT Thermocouple Type T (ID number GG353) interfaced

with an  $\Omega$ EOMEGA calibrator number TC00047-04. This thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. The solutions were prepared by adding an excess of solid salt to water to produce a saturated solution.

**Table 3. Corrections to Temperatures Recorded Using Probes “A” and “B”.<sup>a</sup>**

Recorded Temperature/ °C	Temperature Correction/°C	Temperature Correction/°C
	probe “A”	probe “B”
20	$0.0 - 1.1 = -1.1$	-1.1
30	$-0.0_5 - 1.1 = -1.1_5$	-1.1
40	$-0.1_2 - 1.1 = -1.2_2$	-1.1
50	$-0.1_9 - 1.1 = -1.2_9$	-1.1
60	$-0.2_7 - 1.1 = -1.3_7$	-1.1
70	$-0.3_6 - 1.1 = -1.4_6$	-1.1
80	$-0.4_5 - 1.1 = -1.5_5$	-1.1
90	$-0.5_5 - 1.1 = -1.6_5$	-1.1
100	$-0.6_5 - 1.1 = -1.7_5$	-1.1
110	$-0.8 - 1.1 = -1.9$	-1.1
120	$-0.9 - 1.1 = -2.0$	-1.1
130	$-1.0_5 - 1.1 = -2.1_5$	-1.1
140	$-1.2 - 1.1 = -2.3$	-1.1
150	$-1.3 - 1.1 = -2.4$	-1.1
160	$-1.5 - 1.1 = -2.6$	-1.1
170	$-1.6_5 - 1.1 = -2.7_5$	-1.1
180	$-1.8 - 1.1 = -2.9$	-1.1
190	$-2.0 - 1.1 = -3.1$	-1.1
200	$-2.1_5 - 1.1 = -3.2_5$	-1.1

<sup>a</sup> Probes “A” and “B” are described in the footnotes to Tables 1 and 2. The last digit of some of the numbers in the second column is subscripted. The second figure past the

decimal point is not significant compared to the precision of the determination, but was retained to yield a slightly smoother set of corrections as a function of temperature. The corrected temperatures for the mixed salt system reported in Tables 4 through 6 were rounded off to the nearest 0.1 °C after the corrections were made.

**Table 4. Boiling Temperatures for Saturated Aqueous Solutions of NaCl + KNO<sub>3</sub> + H<sub>2</sub>O.<sup>a</sup>**

x(NaCl)	x(KNO <sub>3</sub> )	pressure (bar)	probe “A” (°C)	temperature/°C corrected
0	1	≈0.99		114.5 <sup>a</sup>
0.0493	0.9507	0.9939	119.98	118.0
0.0533	0.9467	0.9936	119.96	118.0
0.1742	0.8258	0.9940	126.78	124.7
0.2450	0.7550	0.9939	127.75	125.6
0.3157	0.6843	0.9892	136.0	133.8
0.3437	0.6563	0.9893	132.2	130.0
0.3708	0.6292	0.9893	128.5	126.4
0.3992	0.6008	0.9894	124.66	122.6
0.3984	0.6016	0.9947	122.03	120.0
0.4271	0.5729	0.9947	121.99	120.0
0.4372	0.5628	0.9894	122.33	120.3
0.4954	0.5046	0.9947	122.99	121.0
0.6491	0.3509	0.9995	115.87	113.9
1	0	≈0.99		107.7 <sup>b</sup>

Probe “A” is described in footnotes to Tables 1 and 2. <sup>a</sup> This is the average of the five determinations for KNO<sub>3</sub> + H<sub>2</sub>O reported in Table 2. <sup>b</sup> This is the average of three determinations for NaCl + H<sub>2</sub>O reported in Table 2.

**Table 5. Boiling Temperatures for Saturated Aqueous Solutions of NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O.<sup>a</sup>**

x(NaNO <sub>3</sub> )	x(KNO <sub>3</sub> )	pressure (bar)	probe “A” (°C)	probe “B” (°C)	temperature/°C corrected
0	1	≈0.99			114.5 <sup>a</sup>
0.0523	0.9477	0.9918	118.53	117.6	116.5
0.1085	0.8915	0.9918	121.44	120.3	119.3
0.1665	0.8335	0.9919	124.7	123.6	122.6
0.1665	0.8335	0.9951	125.75	124.4	123.5 <sup>b</sup>
0.2205	0.7795	0.9950	129.53	128.0	127.2
0.2729	0.7271	0.9947	133.45	131.8	131.0
0.3334	0.6666	0.9947	138.7	136.9	136.1
0.3619	0.6381	0.9947	146.2	144.7	143.7
0.4329	0.5671	0.9906	157.3		154.8
0.4568	0.5432	0.9957	155.2	153.8	152.7
0.4568	0.5432	0.9964	161.21	160.0	158.8 <sup>b</sup>
0.4568	0.5432	0.9964	161.46	160.3	159.0 <sup>c</sup>
0.4568	0.5432	0.9964	162.40	161.0	159.8 <sup>c</sup>
0.4568	0.5432	0.9968	162.4	160.7	159.7 <sup>c</sup>
0.4569	0.5431	0.9946	156.92	155.4	154.3
0.4569	0.5431	0.9935	163.3	161.5	160.5 <sup>b</sup>
0.4804	0.5196	0.9908	155.9		153.4
0.4982	0.5018	0.9966	154.8		152.3
0.5545	0.4455	0.9912	149.6		147.2

0.6207	0.3793	0.9912	142.73		140.4
0.6895	0.3105	0.9948	134.58		132.4
0.6895	0.3105	0.9914	137.04		134.8 <sup>b</sup>
0.7732	0.2268	0.9949	130.28		128.1
0.8419	0.1581	0.9949	127.30		125.2
0.9007	0.0993	0.9949	124.58		122.5
0.9516	0.0484	0.9949	122.95		120.9
1	0	≈0.994			119.6 <sup>d</sup>

Probes “A” and “B” are described in the footnotes to Tables 1 and 2. <sup>a</sup> This is the average of the five determinations for  $\text{KNO}_3 + \text{H}_2\text{O}$  reported in Table 2. <sup>b</sup> This solution composition is identical to the one given immediately above. These measurements involved dissolution of the glassy solid that was produced when the solution from the previous experiment cooled to room temperature. The observed higher boiling temperatures result because the solid phase in the second determination was a glassy solid solution presumably having a solute mole fraction composition the same as the solution phase. The first boiling temperature obtained in each case, which is generally lower than the value obtained on a subsequent day, was measured after the fresh addition of one or more of the component salts, and should involve a solid solution differing in mole fraction from the solution phase. <sup>c</sup> The first of these boiling temperatures was obtained after dissolving most of the glassy solid from the previous measurements. The second value was determined after the addition of TPFPE boiling stones (which floated on the solution), and the third value after addition of glass beads. The boiling stones and glass beads were added to provide additional nucleation sites for boiling. The concordance of these three boiling temperatures indicates that no superheating was occurring during these boiling temperature measurements. <sup>d</sup> This is the average of five determinations for  $\text{NaNO}_3 + \text{H}_2\text{O}$  reported in Table 2.

**Table 6. Boiling Temperatures for Saturated Aqueous Solutions of NaCl + NaNO<sub>3</sub> + KNO<sub>3</sub> + H<sub>2</sub>O.<sup>a</sup>**

x(NaCl)	x(NaNO <sub>3</sub> )	x(KNO <sub>3</sub> )	pressure (bar)	probe "A" (°C)	probe "B" (°C)	temperature/°C corrected
{moles(KNO <sub>3</sub> )/moles(NaNO <sub>3</sub> )} ≈ 1.01						
0	0.4982	0.5018	0.9966	154.8		152.3
0.1667	0.4152	0.4181	0.9891	173.1		170.3
0.1765	0.4103	0.4132	0.9966	158.2		155.6 <sup>a</sup>
0.1765	0.4103	0.4132	0.9891	168.3		165.6 <sup>b</sup>
0.2580	0.3697	0.3723	0.9892	174.7		171.9
0.3049	0.3401	0.3550	0.9909	182.2		179.3
0.3094	0.3452	0.3454	0.9909	179.8		176.9
0.3192	0.3392	0.3416	0.9892	176.4		173.6
0.3192	0.3392	0.3416	0.9908	176.5		173.7 <sup>b</sup>
0.3616	0.3142	0.3260	0.9909	185.48		182.5
{moles(KNO <sub>3</sub> )/moles(NaNO <sub>3</sub> )} ≈ 1.19						
0	0.4569	0.5431	0.9946	156.92	155.4	154.4
0	0.4569	0.5431	0.9935	163.3	161.5	160.5 <sup>b</sup>
0.0781	0.4212	0.5007	0.9934	176.05	174.5	173.3
0.0781	0.4212	0.5007	0.9907	178.8	177.3	176.0 <sup>b</sup>
0.0781	0.4212	0.5007	0.9928	184.60	182.3 <sub>5</sub>	181.5 <sup>c</sup>
0.0781	0.4212	0.5007	0.9928	192.22	189.9 <sub>0</sub>	189.0 <sup>c</sup>
0.2299	0.3518	0.4182 <sub>5</sub>	0.9923	198.71	196.8 <sub>5</sub>	195.7

0	0.4568	0.5432	0.9957	155.2	153.8	152.7
0	0.4568	0.5432	0.9964	161.21	160.0	158.8 <sup>b</sup>
{ moles(KNO <sub>3</sub> )/moles(NaNO <sub>3</sub> ) } ≈ 1.19						
0.2300	0.3517 <sub>5</sub>	0.4182 <sub>5</sub>	0.9925	191.2	190.7	188.8

<sup>a</sup> This solution is possibly an unsaturated solutions. <sup>b</sup> This solutions are identical to the one given immediately above. These measurements involved dissolution of the glassy solid that was produced when the solution from the previous experiment cooled to room temperature. The observed higher boiling temperatures result because the solid phase in the second determination was a glassy solid solution presumably having a solute mole fraction composition the same as the solution phase. The first boiling temperature obtained in each case, which is generally lower that the value obtained on a subsequent day, was measured after the fresh addition of one or more of the component salts, and should involve a solid solution differing in mole fraction from the solution phase. <sup>c</sup> These two boiling temperatures were obtained by prolonged heating of the glassy solid that was obtained when the previous solution cooled overnight and became completely solid. These boiling temperature differences result from the slow rate as which the glassy solid dissolved

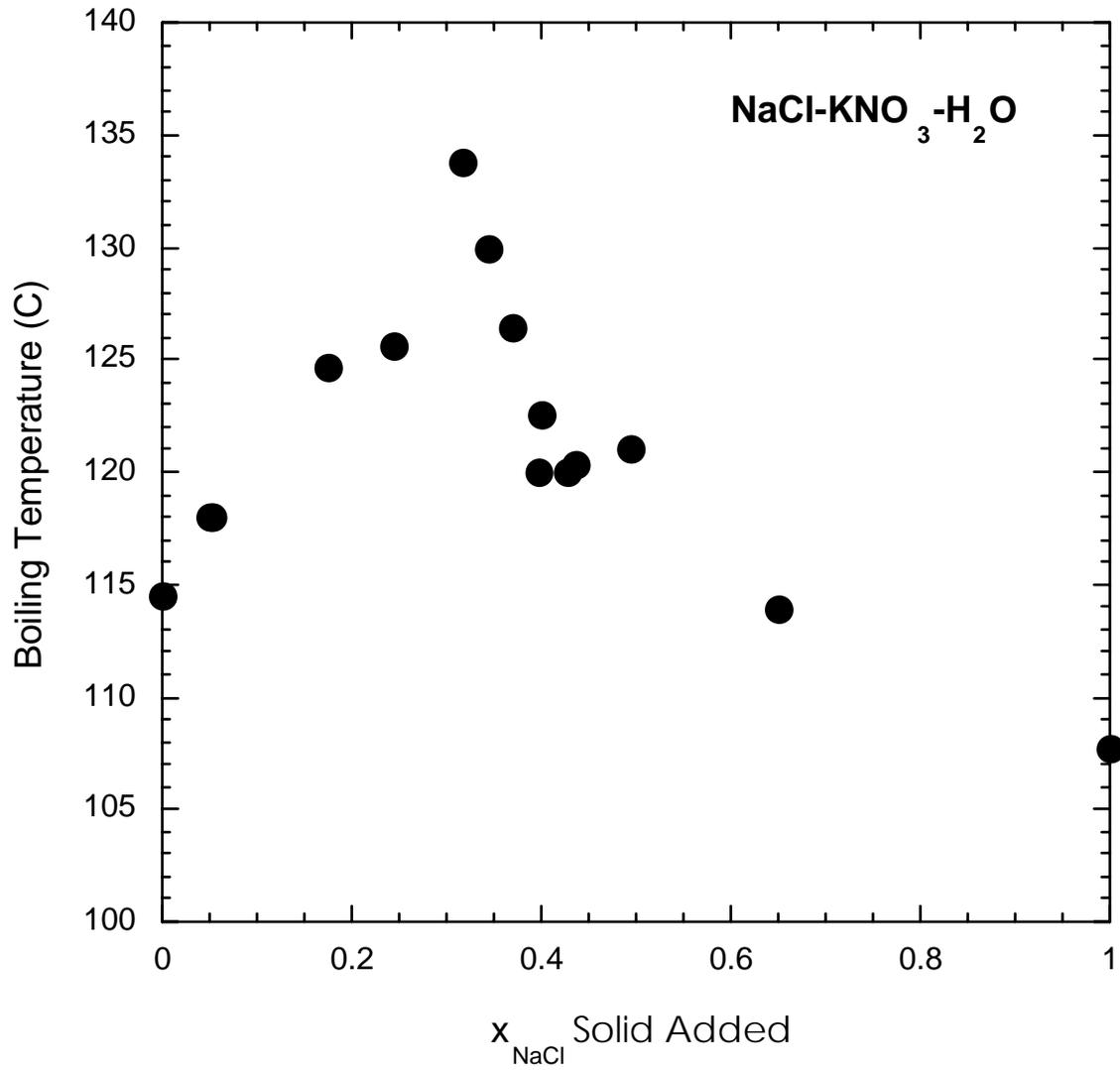


Figure 1: Boiling points measured in the NaCl-KNO<sub>3</sub>-H<sub>2</sub>O system in saturated solutions as a function of the  $x_{\text{NaCl}}$  solid added to the solution.

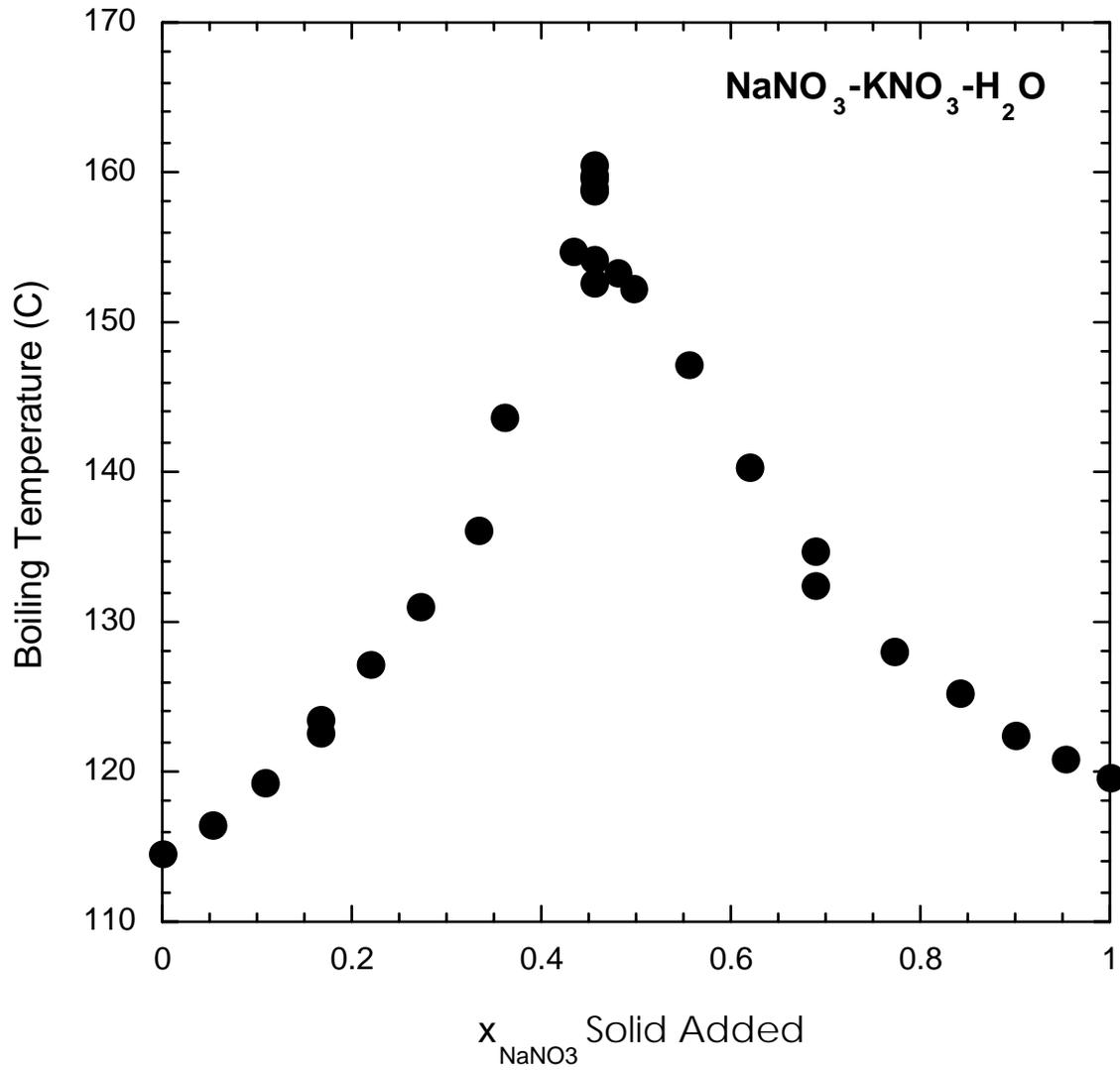


Figure 2: Boiling points measured in the  $\text{NaNO}_3\text{-KNO}_3\text{-H}_2\text{O}$  system in saturated solutions as a function of the  $x_{\text{NaNO}_3}$  solid added to the solution.

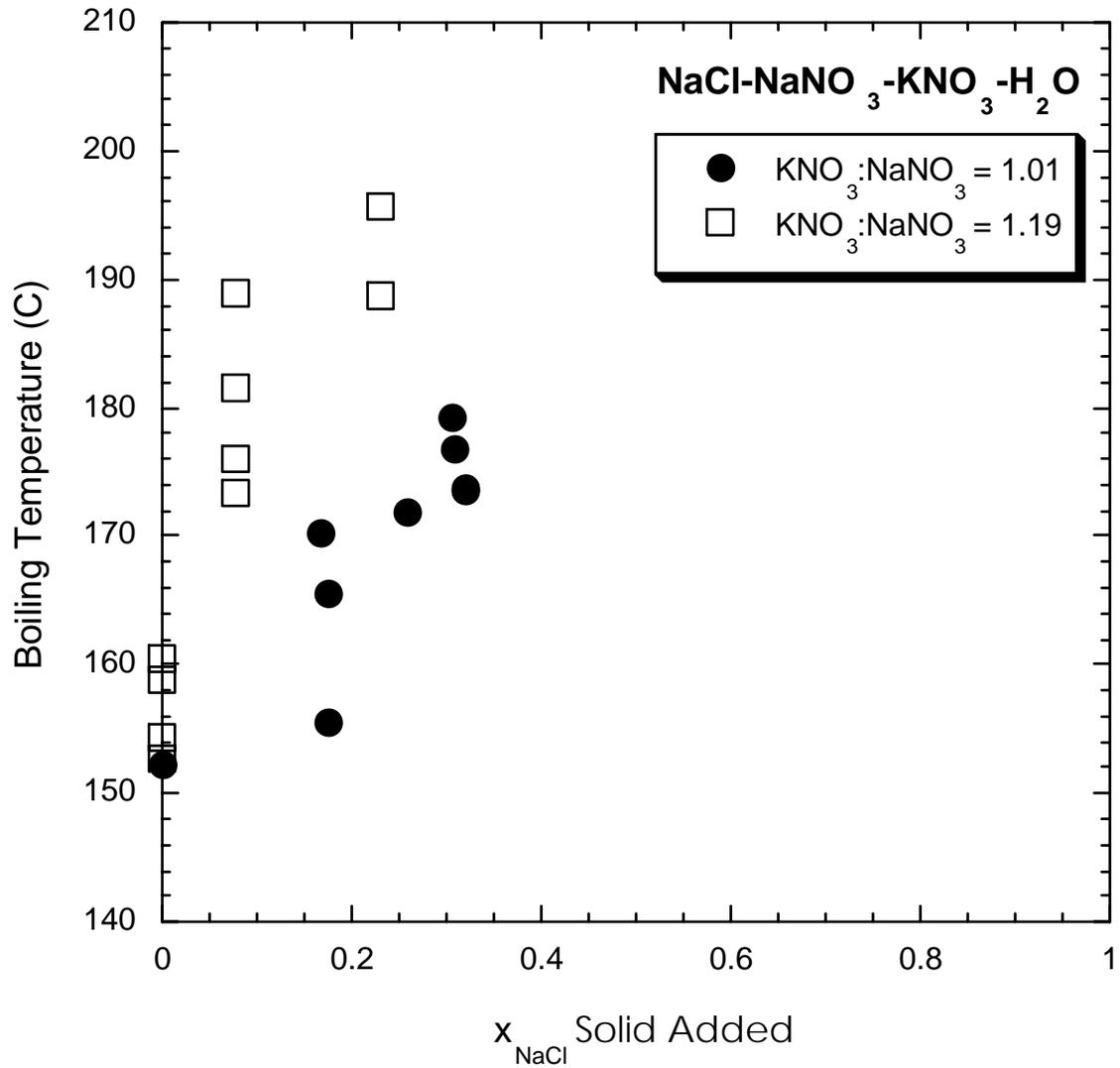


Figure 3: Boiling points measured in the NaCl-NaNO<sub>3</sub>-KNO<sub>3</sub>-H<sub>2</sub>O system in saturated solutions as a function of the  $x_{\text{NaCl}}$  solid added to the solution at two specific mole ratios of KNO<sub>3</sub>:NaNO<sub>3</sub> of 1.01 and 1.19. A KNO<sub>3</sub>:NaNO<sub>3</sub> = 1.19 corresponds to the eutectic ratio of the NaNO<sub>3</sub>-KNO<sub>3</sub>-H<sub>2</sub>O system.

