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Results from Boiling Temperature Measurements for Saturated Solutions in the Systems NaCl + Ca(NO3)2 + H2O, NaNO3 + KNO3 + H2O, and NaCl + KNO3 + H2O, and Dry Out Temperatures for NaCl + NaNO3 + KNO3 + Ca(NO3)2 + H2O

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Results from Boiling Temperature Measurements for Saturated Solutions in the Systems NaCl + $Ca(NO_3)_2$ + H_2O, $NaNO_3$ + KNO_3 + H_2O, and NaCl + KNO_3 + H_2O, and Dry Out Temperatures for NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O

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Abstract

Boiling temperature measurements have been made for saturated ternary solutions of NaCl + KNO_3 + H_2O and $NaNO_3$ + KNO_3 + H_2O at three selected salt ratios and for NaCl + $Ca(NO_3)_2$ + H_2O over the full composition range. The maximum boiling temperature found for the NaCl + $Ca(NO_3)_2$ + H_2O system is 164.7 ± 0.6 °C, and the composition is estimated to occur at $x\{Ca(NO_3)_2\} \approx 0.25$. Experiments were also performed for the five component NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O mixtures with the molar ratio of NaCl:$NaNO_3$:KNO_3 held essentially constant at 1:0.9780:1.1468 as the solute mole fraction of $Ca(NO_3)_2$, $x\{Ca(NO_3)_2\}$, was varied between 0 and 0.25. The NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O system forms low melting mixtures and thus boiling temperatures for saturated were not determined. Instead, the temperatures corresponding to the cessation of boiling (i.e., dry out temperatures) of these liquid mixtures were determined. These dry out temperatures range from ≈300 °C when $x\{Ca(NO_3)_2\} = 0$ to ≥ 400 °C when $x\{Ca(NO_3)_2\} = 0.20$ and 0.25. The investigated mixture compositions correspond to some of the major mineral assemblages that are predicted to control the deliquescence relative humidity of salts formed 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 potential permanent geological repository for the emplacement of high-level nuclear waste. Dust depositing on the upper surface of the waste package will contain contributions both from local particulate material deposited during the construction of the repository, and from dust brought in by ventilation during a cool down period that will also have contributions from atmospheric aerosols. Some of the salts found in this dust could deliquesce and the resulting hot concentrated salt solutions could potentially initiate corrosion of the metallic alloy surface of the waste package. Whether 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 relative and absolute concentrations of the anions Cl^- and NO_3^- will have a major impact on the corrosive ability of these brines.

High nitrate ion concentrations can occur in solutions formed by the evaporative concentration of groundwater whose initial nitrate concentration is low [Rosenberg, Gdowski, and Knauss, 2001; Alai, Sutton, and Carroll, 2005]. Thermodynamic modeling of the deliquescence behavior of the soluble salts leached from dust collected at the Yucca Mountain Repository Site, using EQ3/6 simulations of the evaporation sequence (not including the effect of ammonium ions present in atmospheric aerosols), indicates that the following three salt assemblages are important. Assemblage A consists of the $NaCl + KNO_3 + H_2O$ system, Assemblage B the $NaCl + NaNO_3 + KNO_3 + H_2O$ system, and Assemblage C the $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ system [*Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier*, BSC 2004, DIRS

161237, Table 6.7-11]. The presence of these nitrate salts can considerably reduce the relative humidity at which deliquescence of salt mixtures occurs at high temperatures, as a consequence of their considerable solubility [Linke, 1965]

Reverse deliquescence experiments have been reported for the $NaCl + KNO_3 + H_2O$ and $NaNO_3 + KNO_3 + H_2O$ systems at 90 to 120 °C [Caroll, Craig, and Wolery, 2005]. The measured deliquescence relative humidity (DRH) results agree well with predictions made using the EQ3/6 geochemical modeling code [Wolery and Jarek, 2003] for mixtures with $NaNO_3$ molality fractions $x(NaNO_3) > 0.4$ and $x(NaCl) > 0.4$, but there are significant discrepancies for solutions with $x(KNO_3) > 0.6$. These x values are the solute molality fractions, that is, $x(NaNO_3)$ = (moles of $NaNO_3$)/{(moles of $NaNO_3$) + (moles of KNO_3)} and $x(NaCl)$ = (moles of NaCl)/{(moles of NaCl) + (moles of KNO_3)}; the amount of water is not included when calculating the mole fractions. However, the predicted molalities of the solutions in the vicinity of the eutectic composition are considerably lower than the experimental values.

These significant errors in the model predictions occur because of 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 for $KNO_3(aq)$ are only available at 25 °C, and the $\theta(Cl,NO_3)$ mixing parameter required for modeling the thermodynamic properties of concentrated salt mixtures is similarly only available at 25 °C. Furthermore, modeling calculations for systems containing $Ca(NO_3)_2$ do not converge at temperatures much above 60 °C. At and above 60 °C the ratio of the number of water molecules per ion in a saturated $Ca(NO_3)_2$ solution drops below one, which is outside the intended range of validity of Pitzer's model. The thermodynamic modeling calculations mentioned in the previous paragraph were based on the assumption that the $KNO_3(aq)$ and

θ(Cl,NO_3) Pitzer parameters do not vary with temperature, and their values were assumed to be equal to their known 25 °C values. These severe approximations are expected to give increasingly more serious prediction errors as the temperature is increased because the saturated solution molalities increase rapidly with increasing temperature.

Temperature-dependent KNO_3(aq) binary solution Pitzer parameters and mixing parameter values are needed for improving the thermodynamic modeling predictions but are not yet available. Consequently, in order to understand the behavior of the assemblages at high temperatures, we previously reported boiling temperatures for Assemblage A and B, $NaCl + KNO_3 + H_2O$ and $NaCl + NaNO_3 + KNO_3 + H_2O$, along with the subsystem $NaNO_3 + KNO_3 + H_2O$ [Rard, 2004]. We now report additional boiling temperature measurements for saturated solutions in the $NaCl + KNO_3 + H_2O$ and $NaNO_3 + KNO_3 + H_2O$ systems at three selected salt ratios, for $NaCl + Ca(NO_3)_2 + H_2O$ over the full composition range, and for $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$. The last system corresponds to Assemblage C, and $NaCl + Ca(NO_3)_2 + H_2O$ is one of its subsystems. These measurements directly establish the upper temperature limits at which deliquescence can occur in these salt mixtures, and will provide guides for future geochemical modeling calculations.

2. Experimental Description

All of the experimental measurements and data described in this report are detailed in YMP scientific notebooks SN-LLNL-SCI-474-V4, pages 79 through 158, and SN-LLNL-SCI-474-V6, pages 1 through 41. The data from this report are tabulated in DTN LL050901931032.009.

2.1. The Boiling Temperature Apparatus and the Temperature Measurements

The boiling temperature apparatus was described previously [Rard, 2004] and a summary of that description is given here. The measurements were made using an apparatus constructed from a 1 L flat bottom pyrex kettle to which an upper pyrex 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 control the rate of evaporation of water during the experiments. The shaft of a three-blade propeller stirrer was inserted into 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 as the solution is heated and the solubility changes. 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 normally closed with rubber stoppers during the boiling temperature measurements. One port was opened when dry salts or water were added to this vessel using a plastic funnel, for the visual observation of the boiling of the solution, or when solutions were being concentrated by evaporation of solvent, but otherwise it was closed with a rubber stopper. The other two ports were used for thermocouple probes, which were inserted through the centers of the rubber stoppers. The internal volume of the boiling temperature apparatus was approximately 1 L, of which typically about 200 to 300 mL was occupied by solution and solid during the boiling temperature measurements. The bottom section of the apparatus was surrounded by a heating mantle, with heat being applied separately to the bottom and to the sides of the apparatus.

Two thermocouple probes were present in the solutions during the boiling temperature measurements. The first thermocouple probe was positioned in the solution near the edge of the flask outside the sweep of the propellers of the stirrer. The second thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. Type T thermocouples coated with Teflon were used in the majority of the experiments. However, the temperatures encountered for the NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O system generally exceed 300 °C, and the Teflon coating of the thermocouples melted off during an experiment when the temperature exceeded 350 °C. These two thermocouples were replaced by Type T thermocouples contained in uncoated inconel wells for the remaining NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O experiments. All four thermocouples were calibrated by Heusser Neweigh before and by Bechtel Nevada after the boiling temperature measurements were made. Calibrations done at approximately 0, 100, and 200 °C for the first pair of thermocouples after they were stripped of their Teflon coating agreed with their previous calibration to within 0.1 °C, which is within the uncertainty of the calibration. One of the thermocouples (GG348) was used above its calibrated range for the first three measurements reported in Table 4, 297 to 354 °C. An in-house calibration was made for this temperature probe by Kirk J. Staggs using an Omega hot-point cell and the results are documented in scientific notebook SN-LLNL-SCI-474-V6, pages 40 and 41. The calibration results agreed with the nominal results in this temperature region to within 0.59 to 0.69 °C, which is within the ±0.7 °C uncertainty of the temperature measurements.

The thermocouples were interfaced with a Beamex Multifunctional Calibrator # 009215 or an ΩEOMEGA 450ATT Hand Held Reader. The specific thermocouple(s) and calibrator(s) used are described in the footnotes to Tables 1 through 4. The upper temperature limit for the ΩEOMEGA Hand Held Reader is 204 °C whereas for the Beamex Multifunctional Calibrator it is 400 °C; above these temperatures the temperature readers shut off.

Based on observations given in the previous report [Rard, 2004], the temperature readings from the second thermocouple probe, which is located near the center of the boiling temperature apparatus, are less affected by the temperature gradient between the heating mantle and the solution being investigated. Thus the corrected temperatures reported in Tables 1 through 4 were based on the readings of this second probe, but were adjusted slightly to bring the measured boiling temperatures for water into agreement with literature values [Weast, 1987] as described two paragraphs below.

On three occasions a pyrex kettle cracked after the boiling temperatures were recorded, probably either during cool down or after the apparatus had cooled to room temperature. The cracking may have resulted because of the large temperature changes that occurred during the heating and cooling cycles. However, it is also possible that the salt cake that formed as the solutions cooled could have absorbed moisture from the atmospheric air and swelled, giving rise to stress on the kettle.

Eighteen determinations were made of the boiling temperature of water at ambient pressure. Examination of the critically assessed vapor pressures of water in the Handbook of Chemistry and Physics [Weast, 1987, page D-190] at the recorded pressures allowed the true boiling temperatures to be determined that correspond to the recorded pressures, and these values were compared with the measured boiling temperatures. The observed boiling temperatures were always slightly higher than the correct values, implying that there is a small effect from heat transport limitations even near the center of our boiling temperature apparatus. Accordingly, the nominal boiling temperatures were adjusted downward to yield complete agreement for the boiling temperature of water measured with the second (inner) thermocouple. Because of slight changes in the configuration of the boiling temperature apparatus every time the pyrex kettle was replaced, this temperature correction was redetermined by water calibrations every time the kettle was replaced. The temperature corrections, from first to last, are -0.9_6, -1.0_3, -0.8_0, and -1.4_2 °C.

Based on the size of the temperature corrections (≈ 1 °C), the reproducibility of the boiling temperatures measured for pure H_2O and saturated aqueous solutions of the single salts (Tables 1 and 2), and agreement with boiling temperatures for saturated solutions of the single salts reported in the literature [Timmermans, 1960], the uncertainties in the reported corrected temperatures are estimated to be about 0.5 °C for temperatures around 100 °C and about 1 °C for temperatures around 200 °C. For temperatures much above 200 °C to about 300 °C the uncertainties are around 2 °C. However, for dry out temperatures of $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2$ solutions containing $x\{Ca(NO_3)_2\} \geq 0.05$, the uncertainties are somewhat larger because of difficulty in observing when boiling ceases, and could be as large as 5 to 10 °C.

Teflon boiling chips and/or glass beads were added to the solution in the apparatus to prevent slight superheating. Teflon melts around 350 °C and thus only glass beads were used at temperatures higher than this.

No calibrated pressure measuring system was available for these experiments, so the reported pressure for each experiment is the atmospheric pressure at the Lawrence Livermore National Laboratory (LLNL) site at the time closest to that of a boiling temperature measurement, as reported by the LLNL weather station internet web site (http://www-met.llnl.gov). The LLNL atmospheric pressures are reported and updated every 15 minutes (96 readings each day). The reported pressure at the time closest to an experiment was recorded in the scientific notebooks used for this study.

The boiling point of an aqueous solution is a function of the atmospheric pressure. Boiling occurs when the vapor pressure of water above the solution becomes equal to the ambient (atmospheric) pressure. The atmospheric pressure readings obtained from the LLNL weather site are included in this report to assist in possible future correction of the boiling points reported here to another site, which might have a different range of atmospheric pressure. Atmospheric pressure is a function of elevation, but strong variations can occur due to different weather phenomena.

The atmospheric pressure data included here are considered Established Fact under LP-3.15Q-BSC (Rev 0 ICN 0). Per Attachment 3 of that procedure, Established Fact includes "…numerical data from federal, state, or local government organizations such as the National Weather Service, Census Bureau, or Department of Agriculture." The LLNL weather site is a federal/state facility that obtains and distributes local meteorological data. This facility is independent of the Yucca Mountain Project.

2.2. Source Chemicals and Preparation of the Solutions

The mixtures used for the boiling temperature experiments were prepared by weight using the solid salts and purified water. The source NaCl, $NaNO_3$, and $Ca(NO_3)_2{\cdot}4H_2O$ chemicals used for all of the experiments were supplied in one pound bottles by J. T. Baker ("Baker Analyzed"). J. T. Baker KNO_3 was used in some of the boiling temperature experiments whereas Merck KNO_3 was used in others. The Merck KNO_3 was taken from a 50 kg bulk sample stored in a double plastic bag in its original shipping container.

The salt samples were weighed to a precision of 1×10^{-4} g using an in calibration Sartorius balance (SN80110582, TIP-CM-25-0-1), 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 ≤ 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 with two exceptions. The Merck KNO_3 was coarser grained than the J. T. Baker KNO_3, and the Merck sample showed a slow weight loss for several hours after being removed from the storage container. It was thereafter allowed to equilibrate with the laboratory atmosphere for overnight or longer, which eliminated this problem (presumably the result of drying of small amounts water present in the source chemical). The J. T. Baker $Ca(NO_3)_2{\cdot}4H_2O$ showed similar slow weight changes when removed from the original bottle, presumably indicating the initial presence of a water content slightly greater that of the thermodynamically stable hydrate at this temperature.

The purities of the J. T. Baker NaCl, $NaNO_3$, and KNO_3 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 reported 0.1 % impurities are actually residual water. Dehydration experiments for two commercials 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 ≈500 °C. Thus, for 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. Samples of $Ca(NO_3)_2{\cdot}4H_2O$ from two different lots were used in the experiments with lot analyses of 99.6 and 102.1 %. Because the total amounts of identified elemental impurities did not exceed 0.01 %, the deviations from 100 % $Ca(NO_3)_2{\cdot}4H_2O$ are apparently the result of a deficiency or excess of water. The water activity of a saturated solution in equilibrium with $Ca(NO_3)_2{\cdot}4H_2O$ at 25 °C is $a_w = 0.500$ (Robinson and Stokes, 1965, Appendix 8.11, Table 2), and because the RH in laboratories is typically around this value, the composition of the air dried samples used in the experiments was presumed to be nearly stoichiometric $Ca(NO_3)_2 \cdot 4H_2O$.

The number of moles of each salt were calculated from the sample weights assuming that the molar masses are 58.443 g-mol^{-1} for NaCl, 84.99 g-mol^{-1} for $NaNO_3$, 101.11 g-mol^{-1} for KNO_3, and 236.15 g-mol^{-1} for $Ca(NO_3)_2 \cdot 4H_2O$. 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, $NaNO_3$, and KNO_3 are nearly the same: 2.165 g-cm^{-3}, 2.261 g-cm^{-3}, and 2.109 g-cm^{-3}, respectively, and of $Ca(NO_3)_2 \cdot 4H_2O$ is about 1.9 g-cm^{-3} [Weast, 1987]. 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, which were calculated from the amount of added salt, should be accurate to ≤ 0.2 %. However, as noted elsewhere in this report, the calculated *as added* mole fraction compositions for some of the systems may not correspond to those present in the solution phase because of precipitation of less soluble phases such as KCl.

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. Sample of one or more of the salts were separately weighed using individual plastic weighing boats, and the weighed solid(s) was (were) transferred to the boiling temperature apparatus through an open port. The heaters in the heating mantle were turned on and heating was continued until the solution began boiling (and was concentrated sufficiently, if necessary, until solid phase was present), and then the boiling temperature of the saturated solution was recorded. However, $Ca(NO_3)_2{\cdot}4H_2O$ melts in its own water of hydration, and solutions containing it were evaporated until a solid phase was produced.

2.4. Melting Temperature Determinations

Melting/solidification temperatures were measured by S. Dan Day using differential scanning calorimetry (DSC). These results are documented in notebook SN-LLNL-SCI-474-V4. The measurements were made using a sample of the first mixture reported in Table 4, $NaCl + NaNO_3 + KNO_3$ with *as added* mole fraction of $x\{NaCl\} = 0.32002$, $x\{NaNO_3\} = 0.31299$, and $x\{KNO_3\} = 0.36699$. A sample of the anhydrous mixture was removed while molten and then allowed to solidify before being used for the DTA measurements. An additional sample having essentially the same salt mole fractions was prepared by direct weighing of the anhydrous salts, followed by repeated mixing and grinding to produce a more nearly homogeneous sample. In addition, melting/solidification temperatures were measured for the source $NaNO_3$ and KNO_3 samples.

Temperatures determined on the heating and cooling cycles of the DSC measurements showed some difference from kinetic factors related to thermal conductivity, with the temperatures obtained during the cooling cycle being higher. Comparison of the measured melting temperatures of $NaNO_3$(cr) and KNO_3(cr) to literature values [Linke, 1965; Weast, 1987] indicated that those obtained on the cooling cycle are more accurate due to a smaller thermal lag. The melting temperatures thus determined for the two $NaCl + NaNO_3 + KNO_3$ samples were in good agreement yielding an average of 218 ± 3 °C. This value is very slightly lower than the minimum melting/freezing temperatures of 222 °C reported for the $NaNO_3 + KNO_3$ system [Timmermans, 1960, page 156]. The presence of NaCl apparently has a minimal effect on the minimum melting/freezing temperatures of the $NaCl + NaNO_3 + KNO_3$ system.

3. Results

3.1. Binary Solutions

Timmermans [Timmermans, 1960; pages 306, 307, 387, 388, 554, 555, 778] lists values of the "normal boiling points" of saturated aqueous solutions of various 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 $NaCl + H_2O$ solutions are 108.50, 108.668, and 109 °C; for $NaNO_3 + H_2O$ are 120.20, 121, and 122 °C; for $KNO_3 + H_2O$ are 115.549, 115.9, and 118 °C; and for $Ca(NO_3)_2 + H_2O$ are 151 and 152.0 °C. The last value for saturated $KNO_3 + H_2O$ is presumably an outlier. After taking into account that our experimental pressures reported in Tables 1 and 2 are slightly different than 1 atmosphere (1.01323 bar), our boiling temperatures are in good agreement with those in Timmermans and with the earlier results [Rard, 2004].

3.2. $NaCl + KNO_3 + H_2O$ and $NaNO_3 + KNO_3 + H_2O$ Solutions

Boiling temperatures for the saturated $NaCl + KNO_3 + H_2O$ and $NaNO_3 + KNO_3 + H_2O$ systems were reported previously by Rard [2004] over the full composition range. The plots of boiling temperature against solute mole fraction compositions were based on use of the *as added* mole fraction as calculated from the masses of each solute added to the mixtures. However, these calculated mole fractions may differ significantly from the actual solute mole fractions present in the saturated solutions.

Additional boiling temperature measurements were made for saturated solutions of both systems for mixtures prepared with *as added* solute mole fractions of 0.250, 0.500, and

0.750. These new results are reported in Table 1 and compared with the previous results [Rard, 2004] in Figures 1a and 1b, and the agreement is generally good.

Based on the earlier boiling temperature measurements, Rard [2004] estimated from a plot of boiling temperature *versus* solute mole fraction composition that the maximum boiling temperature composition for saturated solutions in the NaCl + KNO_3 + H_2O system will occur at *as added* mole fractions of x(NaCl) ≈ 0.32 and $x(KNO_3) \approx 0.68$ with a maximum boiling temperature of 133.8 °C. A direct determination of this maximum boiling temperature was made by evaporating a boiling saturated solution with an initial *as added* composition of x(NaCl) ≈ 0.5001 and $x(KNO_3) \approx 0.4999$ until the boiling temperature no longer increased. The directly measured value of 134.9 °C (given in Table 1), with an uncertainty between 0.5–1.0 °C, is in very good agreement with the earlier estimate.

Similarly, Rard [2004] estimated from a plot of boiling temperature *versus* solute mole fraction composition that the maximum boiling temperature composition for saturated solutions in the $NaNO_3$ + KNO_3 + H_2O system will occur at *as added* mole fractions of $x(NaNO_3) \approx 0.46$ and $x(KNO_3) \approx 0.54$ with a maximum boiling temperature of ≈160 °C. A direct determination of this temperature was made by evaporating a boiling saturated solution with an *as added* composition $x(NaNO_3) \approx 0.5001$ and $x(KNO_3) \approx 0.4999$ until the temperature no longer increased. The directly measured value of 165.1 °C (given in Table 1), with an uncertainty between 0.5–1.0 °C, is in satisfactory agreement with the earlier estimate but is higher. The major uncertainty in the earlier estimate arose because it was based on a plot of boiling temperature *versus* the *as added* composition, rather than the true solution composition that is unknown.

3.3. NaCl + $Ca(NO_3)_2$ + H_2O Solutions

Heating $Ca(NO_3)_2\cdot 4H_2O$ caused it to melt in its water of crystallization at ≈ 50 °C yielding a clear solution. The mixtures of $NaCl + Ca(NO_3)_2 + H_2O$ were prepared by adding known masses of solid $Ca(NO_3)_2\cdot 4H_2O$ and NaCl to the boiling temperature apparatus followed by heating of the mixture to evaporate excess water. Heating these mixtures above ≈ 50 °C yielded a clear homogeneous solution without a solid phase. There was no distinct sudden precipitation as the solvent was evaporated by heating to higher temperatures, but rather the boiling solutions first became slightly opaque/turbid and, with further evaporation, became cloudy with a small amount of finely divided solid phase. Upon cooling, these concentrated solutions produced an extremely viscous solution or semi-solid gel phase along with some finely divided solid. Aqueous solutions of $Ca(NO_3)_2$ are known to achieve considerable levels of oversaturation, and usually transform into a gel phase rather that precipitating a crystalline phase. According to the solubility data tabulated in Linke [1958], above about 51 °C the thermodynamically stable solid phase in contact with a saturated solution is $Ca(NO_3)_2(cr)$.

An initial series of experiments was performed for $NaCl + Ca(NO_3)_2 + H_2O$ solutions in which the temperature was recorded when the boiling solutions first took on the distinct cloudy appearance. These boiling temperatures are listed in Table 2. It is apparent from these results that the measured boiling temperature is essentially constant for solutions with *as added* mole fraction compositions falling in the range $0.3000 \leq x\{NaCl\} \leq 0.8000$, 164.7 ± 0.6 °C ($\sigma_{n-1}$ standard deviation). This constancy suggests that all of the solutions in this composition range have evolved to the maximum boiling composition in which both solid NaCl and $Ca(NO_3)_2$ are present. However, in view of the discussion in the preceding paragraph, it can not be stated with certainty whether the $Ca(NO_3)_2$ is present as a crystalline or gel phase.

A second series of experiments was performed in which the temperature was recorded at the time the boiling solutions first took on a slightly opaque/turbid appearance. These results are reported in Table 3 and are plotted in Figure 1c. For these measurements, because only a very small amount of solid phase was present, the *as added* mole fraction compositions should be very close approximations to the true solution mole fraction compositions. It is apparent from Figure 1c that the mixtures with $0.3000 \le x\{\mathrm{NaCl}\} = 1$ form a smooth and continuous curve, as do the measurements with $0.8000 \le x\{\mathrm{Ca(NO_3)_2}\} = 1$. Extrapolation of these two curves indicates they would intersect at $x\{\mathrm{NaCl}\} \approx 0.25$ and $x\{\mathrm{Ca(NO_3)_2}\} \approx 0.75$ with a boiling temperature between 165 and 170 °C.

Comparison of the results from the two series of experiments gives rise to the following interpretation of the measured boiling temperatures. The boiling temperatures of Table 3 for the mole fraction composition range $0.3000 \le x\{\mathrm{NaCl}\} = 1$ correspond to the presence of a solid phase of NaCl(cr). This is supported by the fact that the curve of boiling temperature *versus* $x\{\mathrm{NaCl}\}$ extrapolates smoothly to the boiling temperature of the binary saturated solution of aqueous NaCl as $x\{\mathrm{NaCl}\} \to 1$. Similarly, the boiling temperatures of Table 3 for the mole fraction composition range $0.8000 \le x\{\mathrm{Ca(NO_3)_2}\} = 1$ correspond to the present of a solid phase of $\mathrm{Ca(NO_3)_2(cr)}$, because the boiling temperatures of the mixtures extrapolate smoothly to the boiling temperature of the binary saturated solution of aqueous $\mathrm{Ca(NO_3)_2}$. Furthermore, the temperature at which the two curves shown in Figure 1c intersect occurs right in the range of the maximum boiling temperatures reported in Table 2. Thus the maximum boiling temperature composition for saturated solutions in the $\mathrm{NaCl + Ca(NO_3)_2 + H_2O}$ system occurs at $x\{\mathrm{NaCl}\} \approx 0.25$ and $x\{\mathrm{Ca(NO_3)_2}\} \approx 0.75$ with a maximum boiling temperature of 164.7 ± 0.6 °C.

3.4. $\mathrm{NaCl + NaNO_3 + KNO_3 + H_2O}$ Solutions

An estimate was made of the mole fraction composition at which saturated solutions of $NaCl + NaNO_3 + KNO_3 + H_2O$ will have their maximum boiling temperature, based on the measured boiling temperatures for the $NaCl + KNO_3 + H_2O$ and $NaNO_3 + KNO_3 + H_2O$ subsystems. The maximum boiling composition for saturated solutions in the $NaCl + KNO_3 + H_2O$ system was found to occur at *as added* mole fractions of $x(NaCl) \approx 0.32$ and $x(KNO_3) \approx 0.68$ [Rard, 2004], and it was assumed that the maximum boiling temperature composition will also occur at *as added* mole fraction of $x(NaCl) \approx 0.32$ for $NaCl + NaNO_3 + KNO_3$ mixtures. Likewise, the relative proportions of $NaNO_3$ and KNO_3 in the $NaCl + NaNO_3 + KNO_3 + H_2O$ mixtures was estimated to be 0.46:0.54 from the $NaNO_3 + KNO_3 + H_2O$ boiling temperature measurements. Thus the estimated *as added* mole fraction composition of the maximum boiling temperature saturated three salt system is $x(NaCl) \approx 0.320$, $x(NaNO_3) \approx 0.313$, and $x(KNO_3) \approx 0.367$. Rard [2004] reported boiling temperatures results for saturated $NaCl + NaNO_3 + KNO_3 + H_2O$ solutions with this $NaNO_3/KNO_3$ ratio and with variable mole fractions of NaCl. The boiling temperatures ranged from 154 °C to 196 °C for *as added* mole fractions $x(NaCl) = 0$ to 0.2299 and increased as the mole fraction of NaCl increased, but the measurements did not extend to higher values of $x(NaCl)$.

A mixture was prepared with *as added* mole fraction $x(NaCl) = 0.50002$, which is a much higher mole fraction than for the predicted maximum boiling composition of $x(NaCl) = 0.32$, and it should contain a significant excess of solid NaCl. The measured boiling temperature of 119.8 °C, the last experiment of Table 4, is much lower than observed in the earlier experiments [Rard, 2004], which indicates that the maximum boiling composition for the saturated solutions in the $NaCl + NaNO_3 + KNO_3 + H_2O$ system will occur somewhere within the *as added* mole fraction range $0.230 \leq x(NaCl) < 0.500$.

A solution having the predicted *as added* maximum boiling temperature composition $x(\mathrm{NaCl}) \approx 0.320$, $x(\mathrm{NaNO_3}) \approx 0.313$, and $x(\mathrm{KNO_3}) \approx 0.367$ was also prepared, and heating the mixture gave saturated solutions whose boiling temperatures gradually increased as more solid dissolved. Between about 200 and 260 °C little solid remained, but the solution was opaque (turbid) and boiling vigorously. As the temperature was further increased the rate of boiling decreased and the solution gradually became clear. By 300 °C the boiling has ceased and did not reoccur as the solution temperature was further increased. A repeat experiment with very nearly the same composition gave a very similar temperature of 297 °C when boiling ceased. See the first two experiments of Table 4. As described in Section 2.4, the anhydrous $NaCl + NaNO_3 + KNO_3$ mixture has a melting/freezing temperature of 218 ± 3 °C.

The observations in the preceding paragraph clearly indicate that for the mixture with *as added* mole fractions $x(\mathrm{NaCl}) \approx 0.320$, $x(\mathrm{NaNO_3}) \approx 0.313$, and $x(\mathrm{KNO_3}) \approx 0.367$, any excess $NaNO_3 + KNO_3$ mixture present in the solid phase melts by about 220 °C and the excess NaCl gradually dissolves in the resulting solution as the temperature is further increased, yielding a molten salt mixture containing dissolved water. The observed cessation of boiling at 297–300 °C apparently corresponds to the evaporation of the last water from the molten salt mixture to yield an anhydrous molten salt. Thus, the observed temperatures of 297–300 °C should be considered as the dry out temperature for the $NaCl + NaNO_3 + KNO_3$ system.

3.5. $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ Solutions

As described in the preceding section, the $NaCl + NaNO_3 + KNO_3 + H_2O$ mixture with the *as added* mole fractions $x(\mathrm{NaCl}) \approx 0.320$, $x(\mathrm{NaNO_3}) \approx 0.313$, and $x(\mathrm{KNO_3}) \approx 0.367$ yields a molten salt mixture containing dissolved H_2O that becomes anhydrous when heated to 300 °C. All of the $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ mixtures investigated have the same mole ratio of $NaCl/NaNO_3/KNO_3$, and it is therefore not surprising that all of studied $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ mixtures form molten salts with dissolved water that become anhydrous at high temperatures.

Table 4 lists the dry out temperatures for the $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ mixtures, where the molten salt mixtures are anhydrous above these temperatures. The dry out temperatures increase rapidly with increasing values of $x\{Ca(NO_3)_2\}$, from $x\{Ca(NO_3)_2\} = 0$ to 0.1500. The dry out temperature for the mixtures with $x\{Ca(NO_3)_2\} =$ 0.2000 and 0.2500 are even higher, > 400 °C, but the exact dry out temperatures could not be determined because they exceed the 400 °C upper limit of our temperature measuring system. However, boiling was extremely slow for these solutions at 400 °C, which implies that the dry out temperatures are only slightly higher than this. It should be noted that because the solutions at the dry out temperatures are molten salts, the mole fractions of the solute components are identical to those calculated from the masses of added salt.

4. Summary

Boiling temperature were measured for saturated solutions in the $NaCl + KNO_3 + H_2O$, $NaNO_3 + KNO_3 + H_2O$, and $NaCl + Ca(NO_3)_2 + H_2O$ systems. The observed maximum boiling temperatures for these systems are 134.9 °C, 165.1 °C, and 164.7 ± 0.6 °C, respectively. The uncertainties of the first two boiling temperatures is estimated as being between 0.5 and 1.0 K. Dry out temperatures of $\geq$ 300 °C were also determined for the $NaCl + NaNO_3 + KNO_3 + Ca(NO_3)_2 + H_2O$ system, which correspond to the temperatures at which the molten salt plus water mixture ceases to boil and becomes anhydrous.

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Table 1. Boiling Temperatures for Saturated Aqueous Solutions of NaCl + KNO_3 + H_2O and $NaNO_3$ + KNO_3 + H_2O.[a]

x\{NaCl\}	x\{$NaNO_3$\}	x\{KNO_3\}	pressure/ bar	temperature/°C corrected
1	0	0	0.9895	107.9
1	0	0	0.9875	107.4
1	0	0	0.9854	107.7
1	0	0	0.9820	107.7
1	0	0	0.9882	107.7
0	1	0	0.9941	120.4
0	0	1	0.9967	115.6
0	0	1	0.9967	115.5
0	0	1	0.9986	115.3
0	0	1	1.0005	116.0
0.4999	0	0.5001	0.9869	114.8
0.5001	0	0.4999	0.9921	115.2
unknown	0	unknown	0.9958	134.9[b]
0.5001	0	0.4999	0.9900	120.0[c]
0.7500	0	0.2500	0.9882	110.7
0.2501	0	0.7499	0.9968	126.2
0.2501	0	0.7499	1.0029	126.7[d]
0	0.7500	0.2500	0.9915	129.4
0	0.7500	0.2500	0.9939	129.3[d]
0	0.2500	0.7500	1.0061	129.6
0	0.5001	0.4999	1.0047	163.6

0	unknown	unknown	1.0047	165.1[b]

[a] The reported compositions are the solute mole fractions (not including water) that were calculated from the mass of each solute component added to the solution. Because the amount of solid present is not known, the reported *as added* mixture mole fractions are not accurate reflections of the solution composition. Two thermocouple measuring systems were used for these experiments. Probe “A” consists of an ΩEOMEGA 450ATT Hand Held Reader (serial number 02120180) interfaced with a type T thermocouple (GG353, Bechtel I.D. 10474). 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 Hand Held Reader (serial number 02080420) interfaced with a type T thermocouple (GG348, Bechtel I.D. 10473). This thermocouple probe was inserted into the solution near the center of the flask and above the sweep of the propellers of the stirrer. Only the temperature from Probe “B” was used in calculating the corrected temperature. The uncertainties in the reported corrected temperatures are estimated to be about 0.5 °C for temperatures around 100 °C and about 1 °C for temperatures around 200 °C. [b] The solution immediately above was boiled down until the maximum boiling composition was reached. [c] This is the same mixture as the two experiments immediately above, but with a different amount of precipitate. [d] This is the same mixture as immediately above, but water was added to dissolve most of the solid which was then re-concentrated to yield the saturated solution.

Table 2. Boiling Temperatures for Saturated Aqueous Solutions of NaCl + $Ca(NO_3)_2$ + H_2O.[a]

$x\{NaCl\}$	$x\{Ca(NO_3)_2\}$	pressure/ bar	temperature/°C corrected
0	1	0.9994	150.2
0	1	0.9976	150.2
0.1000	0.9000	0.9976	154.2
0.1996	0.8004	0.9995	159.2
0.3000	0.7000	0.9976	164.4
0.4030	0.5970	0.9973	164.6
0.5000	0.5000	0.9948	164.6
0.6000	0.4000	0.9962	164.8
0.7000	0.3000	0.9991	164.2
0.8000	0.2000	1.0019	165.8

[a] The reported compositions are the solute mole fractions (not including water) that were calculated from the mass of each solute component added to the solution. The initially liquid solutions were heated to evaporate solvent until the appearance of a distinct cloudy appearance due to the formation of a solid phase. Because the amount of solid present is not known, the reported *as added* mole fractions are not an accurate reflections of the solution composition, except when $x\{Ca(NO_3)_2\} = 1$ where only a single solute is present. However, the near constancy of the boiling temperatures for solutions with *as added* compositions in the range $0.3000 \le x\{NaCl\} \le 0.8000$, 164.7 ± 0.6 °C ($\sigma_{n-1}$ standard deviation) suggests that all of these solutions have evolved to the maximum boiling composition. The same two thermocouples were used as described in footnote a of Table 1, although the two ΩEOMEGA 450ATT Hand Held Readers were reversed. The uncertainties in the reported corrected temperatures are estimated to be about 0.5 °C and 1

°C.

Table 3. Boiling Temperatures for Saturated Aqueous Solutions of NaCl + $Ca(NO_3)_2$ + H_2O.[a]

x\{NaCl\}	$x\{Ca(NO_3)_2\}$	pressure/ bar	temperature/°C corrected
0.1000	0.9000	0.9980	155.4
0.2000	0.8000	0.9934	161.2
0.3000	0.7000	0.9995	145.8
0.4000	0.6000	1.0022	126.6
0.5000	0.5000	1.0035	119.8
0.6000	0.4000	1.0029	116.1
0.7000	0.3000	0.9978	113.1
0.8181	0.1819	1.0001	111.2
0.9000	0.1000	0.9965	109.7
0.9500	0.0500	0.9943	109.2
1	0	0.9978	107.4
1	0	0.9943	107.8

[a] The reported compositions are the solute mole fractions (not including water) that were calculated from the mass of each solute component added to the solution. The initially liquid solutions were heated to evaporate solvent until they became slightly opaque (turbid). This corresponds to the beginning of precipitation of a solid phase, and the reported mole fractions should correspond very closely to the actual solution compositions. The same two thermocouples were used as described in footnote a of Table 1, although the two ΩEOMEGA 450ATT Hand Held Readers were reversed. The uncertainties in the reported corrected temperatures are estimated to be about 0.5 °C for temperatures around 100 °C and about 1 °C for temperatures around 200 °C.

Table 4. Maximum Boiling (Dryout) Temperatures for Saturated Aqueous Solutions of NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O (No Solid Phase).[a]

x\{NaCl\}	x\{$NaNO_3$\}	x\{KNO_3\}	x\{$Ca(NO_3)_2$\}	pressure/ bar	temperature/°C corrected
0.32002	0.31299	0.36699	0	0.9927	~300
0.32002	0.31298	0.36700	0	0.9907	~297
0.30401	0.29733	0.34865	0.05001	0.9920	~354[b]
0.30402	0.29733	0.34865	0.05000	0.9896	~315[c]
0.29602	0.28950	0.33948	0.07500	0.9900	~325[c]
0.28802	0.28168	0.33030	0.10000	0.9922	~377[c]
0.27202	0.26603	0.31195	0.15000	0.9935	~393[c]
0.25602	0.25038	0.29360	0.20000	0.9922	≥400[c,d]
0.24002	0.23473	0.27525	0.25000	0.9901	≥400[c,d]
(0.50002)[e]	(0.22999)[e]	(0.26999)[e]	0	(1.0005)[e]	(119.8)[e]

[a] The reported compositions are the solute mole fractions (not including water) that were calculated from the mass of each solute component added to the solution. The molar ratio of NaCl:$NaNO_3$:KNO_3 is essentially constant for all these solutions at 1:0.9780:1.1468 and corresponds to the maximum boiling mole fraction composition estimated from the two salt mixture data. The initial solutions plus solid phase were heated to evaporate solvent, which resulted in a molten salt containing some water. The reported temperatures are the lowest temperatures at which visible boiling ceased. At temperatures slightly above the reported values, the system consists of a clear liquid phase that does not boil, and presumably contains the corresponding anhydrous molten salt mixture. All of the solutes are present in this homogeneous liquid phase, and thus the reported mole fractions should correspond to the actual solution composition. Because it is difficult to observe when boiling ceases, the uncertainties of these dry out temperatures could be as large as 5 to 10 °C. [b] This temperature appears to be anomalously high and may be erroneous. The temperature of this experiment was high enough that the Teflon coatings

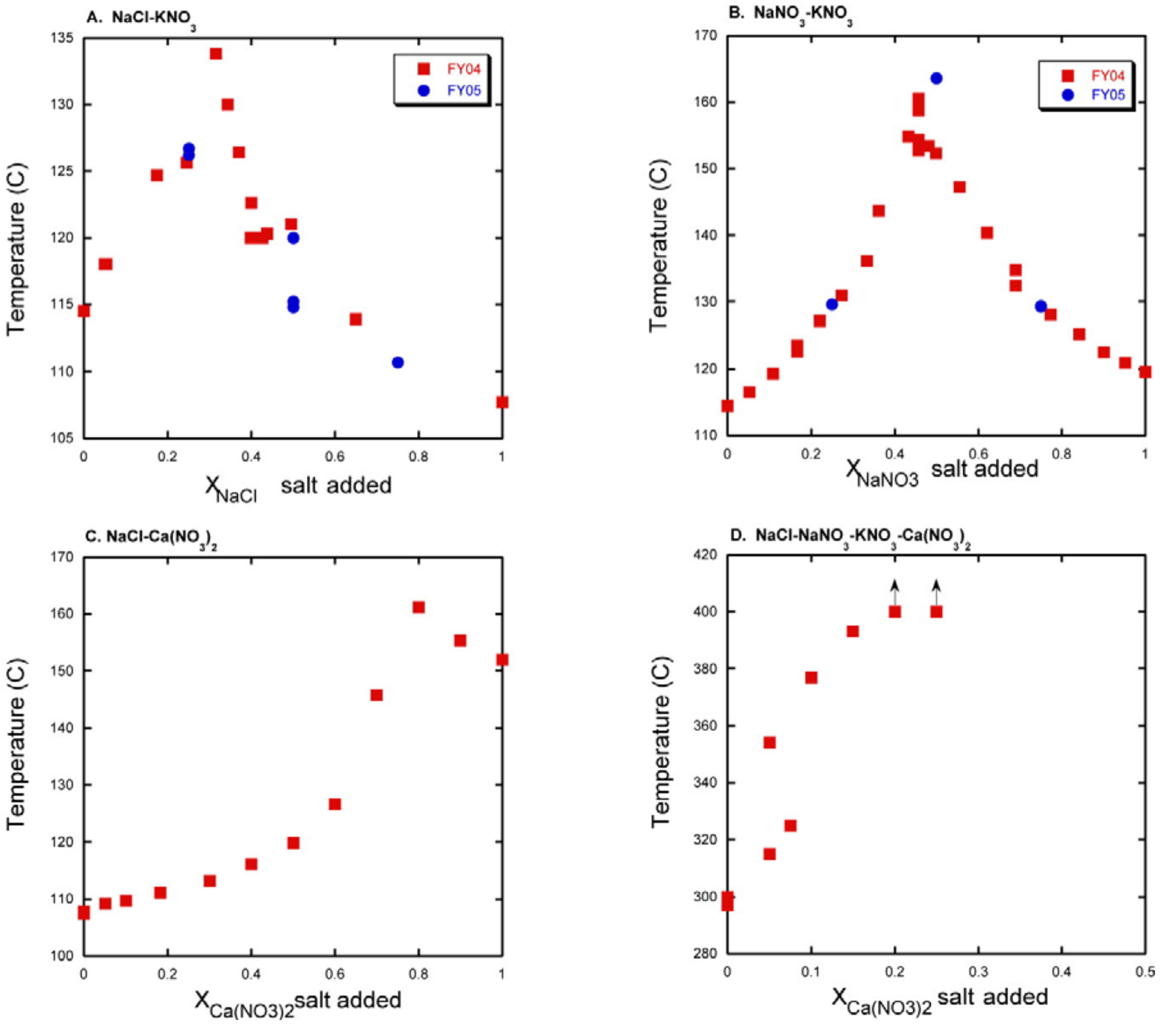
of the Type T thermocouples melted off, although the thermocouples were otherwise undamaged. The following experiment, involving a separately prepared mixture, has a boiling temperature more consistent with the other compositions. [c] The thermocouples for these experiments were type T, but they were uncoated and the thermocouple wells were made of inconel. The I.D. number of the thermocouple used for the reported temperatures is 010164. The reader for the thermocouple used in the experiments reported in this table was a Beamex Multifunctional Calibrator (Bechtel ID 009215). For the first three experiments in this table, the thermocouple was a type T thermocouple (GG348, Bechtel I.D. 10473). [d] These two temperatures are very close to the dry out temperatures at these compositions, but the measuring system being used has a maximum recording temperature of 400 °C. [e]This single experiment is for a different molar ratio of NaCl:$NaNO_3$:KNO_3, with a solid phase in equilibrium with the saturated solution; the other experiments of this table were made above the melting temperature of the salt mixtures.

Figure 1A. Boiling temperatures for saturated NaCl + KNO_3 + H_2O solutions plotted against the mole fraction of NaCl added to the system. Points labeled FY04 (red symbols) are taken from reference [Rard, 2004] and those labeled FY05 (blue symbols) are from the present report.

Figure 1B. Boiling temperatures for saturated $NaNO_3$ + KNO_3 + H_2O solutions plotted against the mole fraction of $NaNO_3$ added to the system. Points labeled FY04 (red symbols) are taken from reference [Rard, 2004] and those labeled FY05 (blue symbols) are from the present report.

Figure 1C. Boiling temperatures from Table 3 for saturated NaCl + $Ca(NO_3)_2$ + H_2O solutions plotted against the mole fraction of $Ca(NO_3)_2$ added to the system (which should correspond closely to the actual solution mole fraction).

Figure 1D. Dry out temperatures NaCl + $NaNO_3$ + KNO_3 + $Ca(NO_3)_2$ + H_2O solutions plotted against the mole fraction of $Ca(NO_3)_2$ added to the system. At these temperatures the system forms anhydrous molten salts.


A. NaCl-KNO$_3$
FY04
FY05
Temperature (C)
135
130
125
120
115
110
105
0
0.2
0.4
0.6
0.8
1
X$_{NaCl}$ salt added
B. NaNO$_3$-KNO$_3$
FY04
FY05
Temperature (C)
170
160
150
140
130
120
110
0
0.2
0.4
0.6
0.8
1
X$_{NaNO3}$ salt added
C. NaCl-Ca(NO$_3$)$_2$
Temperature (C)
170
160
150
140
130
120
110
100
0
0.2
0.4
0.6
0.8
1
X$_{Ca(NO3)2}$salt added
D. NaCl-NaNO$_3$-KNO$_3$-Ca(NO$_3$)$_2$
Temperature (C)
420
400
380
360
340
320
300
280
0
0.1
0.2
0.3
0.4
0.5
X$_{Ca(NO3)2}$ salt added