

Thermodynamics of Molten Salt-Water Mixtures. I. Solubility of Water Vapor in a Potassium Nitrate-Sodium Nitrite Melt

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The solubilities of water vapor at partial pressures of 5 to 24 Torr in a melt containing 55.5 wt % potassium nitrate and 44.5 wt % sodium nitrite have been measured at nine temperatures in the range 143–279°, using nitrogen at atmospheric pressure as a carrier gas. The dependence of the Henry's law constant, K , mole of water (mole of melt)⁻¹ Torr⁻¹, on absolute temperature, $T^\circ\text{K}$, is given by the equation $\ln K = 3.4917 \ln T + 6040/T - 31.4638$. The partial molal enthalpy, entropy, and heat capacity of water at infinite dilution in the melt are derived from this equation and interpreted in terms of strong cation-water bonding.

Introduction

The study of solutions of inorganic salts in water is currently being extended to regions of high temperature and high salt concentration.^{1,2} In particular, thermodynamic data are urgently required for the hot, strong solutions used in chemical processes such as hydrothermal extraction. Furthermore, it appears that improved theories of the structure and properties of electrolyte solutions may come from a study of the molten salt end of the concentration range.^{1,2}

The present work forms part of a study of the complete thermodynamic properties of a model molten salt-water system over the entire concentration range. The salt selected was the 55.5 wt % KNO_3 -44.5 wt % NaNO_2 mixture which forms a congruently melting solid solution of mp 141°. Experience with this salt as an industrial heat transfer medium showed that it forms stable liquid mixtures with water in all proportions under moderate pressures. In contact with normal atmospheres containing water vapor the melt dissolves up to 0.2 wt % water. This concentration region was chosen for initial study because interactions between water molecules in the melt may be considered negligible compared to ion-water interactions. This is the "infinite dilution" approach which has proved so useful at the other end of the salt-water concentration range.

There have been a number of recent studies of water vapor solubility in melts.^{2,4} In all cases Henry's law is obeyed, the solubility being proportional to pressure, and in low-melting salts at least the water appears to retain molecular identity in the melt. However, all work so far reported has been of insufficient precision or covered a temperature range inadequate for the evaluation of reliable thermodynamic properties. The present work aimed to obtain accurate values of enthalpy, entropy, and heat capacity for water at infinite dilution in the 55.5 wt % KNO_3 -44.5 wt % NaNO_2 melt.

Thermodynamics

The system studied consists of a molten salt containing low concentrations of water and nitrogen in equilibrium with a gas phase containing water and nitrogen. The molten salt has negligible vapor pressure and, although a mixture, may be treated as a single component. On approaching infinite dilution of a solute it is empirically found that the mole fraction in the liquid, x , is proportional to the fugacity, f , in the gas phase

$$x = Kf \quad (1)$$

This is a statement of Henry's law, which applies independently to all solutes present at sufficiently low concentration. For the low partial pressures used here, 5–24 Torr water vapor and 760 Torr nitrogen, the fugacity may be replaced by the partial pressure, P . Also, for the low concentrations used, the mole fraction may be replaced by mole ratio, r , in units of moles of solute per (moles of KNO_3 + moles of NaNO_2), giving

$$r = KP \quad (2)$$

This relation has the advantage of applying empirically to higher concentration limits⁵ than eq 1 and is more convenient to use with multiple solutes.

Data of sufficient accuracy relating the Henry's law constant, K , and absolute temperature, T , may be fitted by the relation

$$\ln K = a/T + b \ln T + c \quad (3)$$

(1) J. W. Cobble, *Science*, **152**, 1479 (1966).

(2) J. Braunstein, *Inorg. Chim. Acta Rev.*, **2**, 19 (1968).

(3) M. Ya. Kagan and N. J. Kamuischan, *J. Appl. Chem. (USSR)*, **5**, 347 (1932).

(4) R. Battino and H. L. Clever, *Chem. Rev.*, **66**, 395 (1966).

(5) T. B. Tripp and J. Braunstein, *J. Phys. Chem.*, **73**, 1984 (1969).

Application of the van't Hoff equation⁶ to (3) gives the partial molal enthalpy of solution

$$\overline{\Delta H} = -Ra + RbT \quad (4)$$

where R is the gas constant. Differentiation of (4) with respect to temperature⁶ gives the partial molal heat capacity of solution

$$\overline{\Delta C_p} = Rb \quad (5)$$

which is assumed independent of temperature over the experimental range in this treatment. Assuming that Henry's law extends to infinite dilution, the partial molal enthalpy and heat capacity refer to infinite dilution also.

The partial molal entropy of solution is given by

$$\overline{\Delta S} = \overline{\Delta H}/T \quad (6)$$

It is useful to consider also the change in partial molal entropy due to the change in water concentration from gas (P/RT) to solution (KPd/M)

$$\overline{\Delta S_c} = R \ln (M/KRTd) \quad (7)$$

where M is the mean molecular weight of the melt, d the melt density, and R the gas constant in appropriate units. The difference $\overline{\Delta S} - \overline{\Delta S_c}$ then refers to the solution process without concentration change.

The activity coefficient of water in the melt may be defined by

$$\gamma = P/xP_w^0 \quad (8)$$

where P_w^0 is the vapor pressure of pure liquid water at the temperature considered.

Experimental Section

The materials used were Analar reagent grade potassium nitrate and sodium nitrite, air dried at 150°, and mixed in the proportion 55.5:44.5 by weight. The mix was premelted to give a clear pale yellow melt with a freezing point of $141 \pm 0.5^\circ$. Samples of 40 g were held in a Pyrex saturator containing a sintered glass gas distributor, thermocouple well, and spray trap. Nitrogen bubbled through the melt at $25 \text{ cm}^3 \text{ min}^{-1}$ after passing in series through two water saturators and a spray trap held in a water bath controlled to $\pm 0.01^\circ$. A series of water vapor pressures was obtained using analyzed H_2SO_4 solutions in the saturators. The gas was shown to be fully saturated by measuring the weight of water absorbed in drying tubes from a known volume of saturated gas. Saturation of the melt was continued for 16 hr although tests showed no further uptake of water after 5 hr under the conditions used. The pressure of the gas leaving the final saturator and of that leaving the melt were measured to 0.1 Torr with a calibrated capsule gauge.

After saturation, dry nitrogen was passed to strip water from the melt and collect it in two drying tubes containing magnesium perchlorate. Drying was nor-

mally completed in 4–5 hr after which a small continuous carryover from the melt was observed, attributed to spray, decomposition, vapor pressure of the melt, and traces of water in the dry nitrogen. Blank runs established a correction of 0.08 mg/hr which was applied to all runs independent of temperature. The drying tubes could be reproducibly weighed to 0.1 mg provided they always contained nitrogen at the same temperature and pressure. The weighing error thus varied from 0.1% at 150° to 1% at 280°. Further blank runs without melt in the saturator enabled the water vapor in the 50 cm^3 gas spaces between melt and drying tubes to be accounted for, giving corrections of 1–2 mg with an accuracy of 0.1 mg, depending on temperature, water vapor pressure, and melt volume. A check on overall operation was made by passing dry nitrogen through the melt at 280° and injecting 10.0 ± 0.05 mg of water into the inlet with a microsyringe through a rubber seal. All the water thus passed through the melt was collected again in the drying tubes within 3 hr.

The saturator was held in a well-lagged furnace, with a proportional controller giving better than $\pm 0.1^\circ$ constancy over the period of a run. Temperatures were measured at the center of the melt with a Pt–Pt–13% Rh thermocouple which was calibrated *in situ* at the freezing points of tin and lead to give an accuracy of 0.1° . Tests showed that the gas stream caused negligible cooling of the melt and produced good temperature uniformity. The temperatures of the solubility runs were chosen in random order, and the melt showed no detectable change in color or freezing point and negligible alkalinity.

Throughout this paper $1 \text{ cal} = 4.184 \text{ J}$ and $1 \text{ Torr} = (101.325/760) \text{ KNm}^{-2}$.

Table I: Solubility of Water in 55.5 Wt % KNO_3 –44.5 Wt % NaNO_2 Melt

Temp, °C	Melt, g	Water, mg	Cor-rection, mg	P_w , Torr	$K \times 10^5$, mol of water (mol of melt) ⁻¹ Torr ⁻¹
142.9	44.05	116.4	2.2	19.76	61.0
149.8	44.05	100.2	2.15	19.74	52.4
160.1	44.55	75.2	2.05	19.65	38.1
180.8	44.55	46.5	1.95	19.63	24.2
201.0	44.55	33.3	1.85	19.65	16.7
220.9	44.05	23.1	1.75	19.91	11.3
239.8	44.55	17.0	1.65	19.76	8.12
260.1	44.55	12.7	1.5	19.76	5.92
278.5	44.55	10.1	1.4	19.65	4.62

(6) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1961.

Results

In Table I are listed for nine solubility runs the temperature at the end of saturation, the weight of dry melt introduced, and the weight of water collected on stripping, corrected for carryover (see Experimental Section). A further correction is next listed for water vapor in the gas space above the melt. The partial pressure of water vapor, P_w' , in the gas leaving the final water saturator was obtained from published data⁷ for the relevant temperature and composition of the saturator solution. This was then corrected for expansion through the sintered glass bubbler in the melt and the head of melt. The mean partial pressure of water vapor in contact with the melt was calculated from

$$P_w = (P_A + 0.5H)P_w'/P_B \quad (9)$$

where P_A is the pressure after the melt, P_B the pressure after the final water saturator, and H the static head of melt above the bubbler outlet. It is assumed that there is a slight concentration gradient of water in the melt due to the head in spite of the melt circulation, but this has at most only 0.5% effect on the solubility.

A test of Henry's law was made at several temperatures using water vapor pressures in the range 5–24 Torr. In all cases solubility was proportional to pressure within this range as generally found for water in molten salts.² In Table I Henry's law constants are given for temperatures from just above the freezing point to 280°, above which the precision was inadequate due to the small weight of water collected. The plot of $\log K$ vs. $1/T$ given in Figure 1 has a significant curvature as predicted by eq 3 for a finite change in partial molal heat capacity on solution. The relationship corresponding to eq 3 found by the method of least squares

$$\ln K = 6040/T + 3.4917 \ln T - 31.4638 \quad (10)$$

gives a mean deviation in K of $\pm 1.6\%$. The enthalpy and entropy of solution, calculated from (4), (6), and (7) for three rounded temperatures within the experimental range, are given in Table II. For this purpose

Table II: Partial Molal Enthalpy and Entropy of Solution of Water in 55.5 Wt % KNO_3 -44.5 Wt % NaNO_2 Melt

Temp, °C	$\Delta\bar{H}$, kcal mol ⁻¹	$\Delta\bar{S} - \Delta\bar{S}_0$, cal deg ⁻¹ mol ⁻¹	S_f^a , cal deg ⁻¹ mol ⁻¹
150	-9.1	-10.0	11.50
200	-8.7	-9.1	11.83
250	-8.4	-8.2	12.13

^a From ref 19.

the melt density was obtained by interpolation of published data⁸ on KNO_3 - NaNO_2 mixtures to give

$$d = 2.043 - 6.65 \times 10^{-4}t \quad (11)$$

The solubilities reported here refer to a melt saturated with nitrogen under atmospheric pressure. Provided the water and nitrogen are both at concentration low enough for Henry's law to apply, their solubilities should be independent. The nitrogen concentration may be estimated by an extrapolation of published data for nitrogen in molten sodium nitrate⁹

$$\log K_{N_2} (\text{mol cm}^{-3} \text{ atm}) = 597/T - 6.64 \quad (12)$$

The concentrations calculated from (11) combined with molar volumes of the present melt give nitrogen solubilities of 2.7×10^{-4} mol of N_2 (mol of melt)⁻¹ at 140° and 1.2×10^{-4} mol of N_2 (mol of melt)⁻¹ at 280°. By comparison with data in Table II these represent 2% at 140° and 12% at 280° of the water contents. Under these conditions the nitrogen should have a negligible effect on the water solubility.

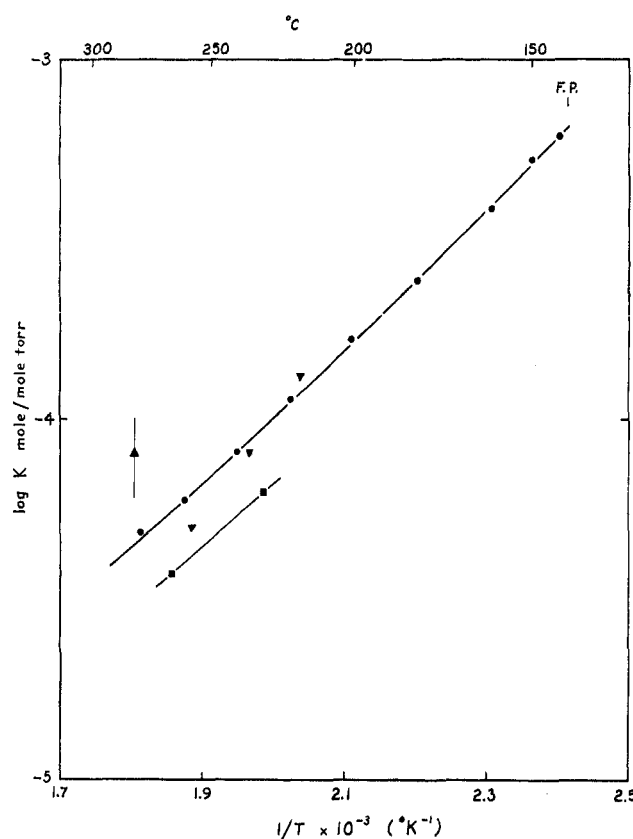


Figure 1. Temperature dependence of solubility of water vapor in various molten salts: ●, present work, 55.5 wt % KNO_3 -44.5 wt % NaNO_2 ; ▼, ref 11, 54 wt % KNO_3 -39.5 wt % NaNO_2 -6.3 wt % NaNO_3 ; ▲, ref 12, NaNO_2 ; ■, ref 16, KNO_3 .

(7) R. H. Stokes and R. A. Robinson, *Ind. Eng. Chem.*, **41**, 2013 (1949).

(8) V. D. Polyakov and S. I. Berul, *Izv. Sektora Fiz. Khim. Analiza Inst. Obshch. Neorgan. Khim. Akad. Nauk SSSR*, **26**, 164 (1955).

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Another factor requiring consideration is the slight hydrolysis of sodium nitrite over long periods, producing sodium hydroxide. Titration of melt samples with acid showed a gradual buildup of alkalinity to a value of 4×10^{-4} equiv/mol (0.02 wt % NaOH) at the end of the solubility runs. This amount would have negligible effect on the solubility of water, and it is known¹⁰ that sodium hydroxide has negligible vapor pressure and decomposition pressure at the temperatures used here. The water injection tests (see Experimental Section) showed that water itself may be reversibly added to and removed from the melt.

In Figure 1 are shown three values of water vapor solubility in a heat transfer melt (54 wt % KNO_3 , 39.5 wt % NaNO_2 , 6.3 wt % NaNO_3). These were calculated from the boiling points¹¹ of this melt containing 0.8, 1.28, and 2.08 wt % water, assuming that Henry's law is obeyed up to these relatively high concentrations. The agreement with the present work is good, but no significance should be attached to the trend with temperature in view of the approximate nature of the measurements and derivation.

The solubility of water vapor in molten sodium nitrite at partial pressures of 7 and 19.5 Torr has been determined cryoscopically.¹² Assuming ideal behavior and a heat of fusion of 2.48 ± 0.07 kcal mol⁻¹, the freezing point depressions gave solubilities of 6×10^{-5} and 1.0×10^{-4} mol (mol of NaNO_2)⁻¹ Torr⁻¹, respectively, at 281°. Similarly, a cryoscopic study¹³ of water in potassium nitrate, when reevaluated using the most recent heat of fusion,¹⁴ 2.413 kcal mol⁻¹, gives a solubility of $(2.0 \pm 0.2) \times 10^{-5}$ mol (mol of KNO_3)⁻¹ Torr⁻¹ at 335°. Other workers¹⁵ used a method of saturation with pure steam and stripping with nitrogen to obtain solubilities of (2.0 ± 0.7) and $(1.5 \pm 0.7) \times 10^{-5}$ mol (mol of KNO_3)⁻¹ Torr⁻¹ at 335 and 360°, respectively. The agreement of the two sets of data for potassium nitrate at 335° suggests that Henry's law applies up to a pressure of 760 Torr, but this may be fortuitous. Further data for potassium nitrate may be derived from solubilities in potassium nitrate-lithium nitrate mixtures,¹⁶ measured directly with a microbalance at water vapor pressures up to 30 Torr. Data for 25, 50, and 75 mol % mixtures may be extrapolated by a smooth curve to give 6.3 and 3.7×10^{-5} mol (mol of KNO_3)⁻¹ Torr⁻¹ at 230 and 265°, respectively. As seen in Figure 1, the present data for a 54 mol % sodium nitrite-46 mol % potassium nitrate melt falls roughly midway between the literature data for sodium nitrite and potassium nitrate.

Discussion

The fact that water solubility in the melt considered here is proportional to the partial pressure suggests simple solution without dissociation or association of the molecule. In contrast, water solubility in halides, silicates, and borates at higher temperatures is propor-

tional to the square root of pressure suggesting dissociation,² while water solubility in organic solvents above a concentration of about 0.05 *M* deviates from proportionality to partial pressure due to association of water molecules.¹⁷

The activity coefficients of water in the melt, relative to the liquid water standard state, vary from 0.55 at 150° to 0.45 at 280°. These figures suggest that the water-melt system is relatively ideal. In the water-lithium nitrate system¹⁶ the water activity coefficient is only 0.13 at 265–280°. On the other hand, a value as high as 12 is observed in a water-liquid paraffin (mean molecular weight 345) mixture¹⁸ at 150°. The activity coefficients reflect the free energy of the water-solvent interactions relative to those in pure water and thus depend on both enthalpy and entropy of bonding of water to the solvent species.

The solution of water in the 55.5 wt % KNO_3 -44.5 wt % NaNO_2 melt is strongly exothermic (Table II). The partial molal enthalpy of solution of -8.4 kcal mol⁻¹ at 250° compares quite well with values of -8.1 kcal mole⁻¹ for potassium nitrate and -9.9 kcal mol⁻¹ for sodium nitrate at 230–265°, obtained by extrapolation of water vapor solubilities¹⁶ in mixtures of these salts with lithium nitrate. The partial molal enthalpy of solution is almost equal to the enthalpy of condensation to liquid water at the same temperature. Thus the nearly ideal behavior results mainly from the similar enthalpy of ion-water interactions in the melt and water-water interactions in liquid water. In such solutions the ion-water interactions² include cation-permanent dipole and cation-induced dipole forces as well as anion-water hydrogen bonding. By comparison, the enthalpy of solution of nitrogen in molten sodium nitrate⁹ is -2.7 kcal mol⁻¹ over the range 355–454°. A small endothermic enthalpy is expected for both solutions due to expansion of the solvent to accommodate the solute, but for nitrogen the strong ion-permanent dipole forces are missing, leading to a less exothermic solution. For the water-paraffin mixture an even lower enthalpy of solution of -1.8 kcal mol⁻¹ at 150° is observed,¹⁸ since here there are

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only the weak dispersion forces acting between non-charged molecules and possibly weak hydrogen bonding.

There is also a large negative change in the partial molal entropy of water on solution in the melt (Table II). Since correction has been made for the entropy due to the change in concentration from gas to melt, ΔS_c , this reduction of entropy must be attributed to changes in the translational or rotational motions of the molecule, the vibrational motions making negligible contribution to the entropy. The rotational entropy, S_r , of the free water molecule, calculated by statistical mechanical methods,¹⁹ is given in Table II. This term alone is of sufficient magnitude to account for the observed entropy of solution. The tight bonding of water molecule to cations suggested by the enthalpy of solution could lead to a loss of most of the rotational entropy of the gas molecule. At more elevated temperatures the increasing thermal energy would then cause increased libration about the lowest energy orientation so that less of the rotational entropy would be lost. The decrease in the ratio $(\Delta S - \Delta S_c)/S_r$ with rise in temperature supports this theory.

The change in the partial molal heat capacity of water from vapor to solution is $6.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$. Although ΔC_p probably varies with temperature, the solubility data are not of sufficient accuracy to reveal this. Since the heat capacity of water vapor¹⁹ is $8.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$, almost independent of temperature within the range considered, the partial molar heat capacity of water at infinite dilution in the melt is $14.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$. This is significantly less than the heat capacity of liquid water²⁰ in the same temperature range, $18.6\text{--}22.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The difference may be attributed to the contribution of the hydrogen bond network to heat capacity in water as well as to a restriction of the rotational heat capacity of water bonded to cations in the melt.

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The Palladium-Catalyzed Carbon Monoxide Oxidation.

Catalyst "Break-in" Phenomenon

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The break-in period for CO oxidation over pressed-disk catalysts of silica-supported palladium was investigated. Kinetic parameters and infrared spectra of adsorbed CO were monitored during this period. At various stages of break-in, the reaction was interrupted and spectra of chemisorbed CO at 35° were determined in the absence of oxygen. Break-in did not commence until the catalyst was exposed to O_2 . For a stabilized catalyst, the apparent activation energy was 15 kcal/mol lower and the apparent preexponential a factor of 10^7 lower than the values observed prior to break-in. Apparent discrepancies in literature values of peak frequencies were correlated with the state of the catalyst with respect to break-in. The break-in phenomenon was interpreted as arising from a redistribution of surface structures resulting from surface diffusion of palladium.

Introduction

The activity of a freshly prepared catalyst almost invariably changes with time in use. Three regimes can usually be identified: a break-in period during which the change (increase or decrease) in activity is relatively rapid and sometimes erratic; a steady-state period during which the activity is relatively constant with time; and a deactivation period. The third

regime is sometimes associated with catalyst poisoning and/or aging and is well documented in the literature for many systems.

Break-in is so commonly exhibited by catalysts that it is rarely reported in the literature. However, very few quantitative studies have been made of break-in and, hence, the phenomenon is not clearly understood. It may be the result of removal of a contaminant or