MOLAR ENTHALPY AT FIVE COMPOSITIONS IN THE NaNO₃–NaOH SYSTEM IN THE LIQUID AND SOLID STATES

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ABSTRACT

The molar enthalpies of the two compounds and three eutectics in the NaNO₃–NaOH system were determined over the 450–630 K temperature range by means of drop calorimetry. The enthalpy changes over the 500–550 K range, which in all cases includes melting, are usefully large from the viewpoint of energy storage: 5.7 (79), 5.2 (83), 5.1 (87), 5.1 (93) and 3.5 (73) kcal mole^{-1} (cal g^{-1}) in 0.710 NaNO₃·0.290 NaOH, 0.500 NaNO₃·0.500 NaOH, 0.411 NaNO₃·0.589 NaOH, 0.327 NaNO₃·0.673 NaOH and 0.178 NaNO₃·0.822 NaOH, respectively. At $\chi_{NaOH} = 0.822$, a high, negative heat of mixing (0.7–0.8 kcal mole^{-1}) was noted. This is contrary to what has been observed in other common cation–mixed anion molten salt solutions.

INTRODUCTION

The NaNO₃–NaOH system is interesting from the viewpoint of heat storage, having three eutectics with relatively low melting points (519, 539 and 531 K) and being fairly easy to contain. A number of groups have considered it for application in this field [1,2].

In view of the sketchiness of available data, we made a survey of the whole system, determining molar enthalpies in the solid and liquid states at each of the three eutectics and also at the two intermediate compounds. In so doing, some rather interesting results for heats of mixing in the liquid state were also obtained.

EXPERIMENTAL

The calorimetric method has been described earlier [3]. MgO crucibles were used for some of the determinations on the four compositions richest in NaNO₃. Stainless steel was also used for these compositions and was used

exclusively for the NaOH-rich composition and for several determinations (for reference purposes) on NaOH. Only very minimal attack was noted. Analytical grade reagents were used. The $NaNO_3$ was dried at about 380 K in air. The NaOH pellets were dehydrated under vacuum, the temperature being raised slowly to about 420 K. Although they were obtained from a newly opened reagent bottle, they underwent a slight change of appearance and a small weight loss under this treatment. Exposure to air caused them to revert to their original state. They were therefore kept in a closed bottle inside a desiccator. When required, they were weighed out as rapidly as possible, and the loaded crucible was immediately suspended in the hot furnace (at no less than 420 K). The method established earlier employed open crucibles and this practice was continued in the present work despite the danger of carbonate formation. It was decided that the amount formed would be small since the CO_2 content of air is low and, in any case, circulation of air around the crucible is restricted by the insulation at each end of the tube furnace. In addition, once the material was molten, it presented only a small surface to the atmosphere. Finally, the primary aim of this work was the production of results of practical value. Accordingly, only normal measures were taken to purify, dry and protect the salts.

Enthalpy was measured at temperatures on either side of the melting points at five compositions corresponding to the two intermediate compounds ($NaNO_3 \cdot NaOH$ and $NaNO_3 \cdot 2\,NaOH$) and the three eutectics (0.710 $NaNO_3 \cdot$ 0.290 NaOH, 0.411 $NaNO_3 \cdot$ 0.589 NaOH and 0.178 $NaNO_3$ $\cdot$ 0.822 NaOH) as read from the phase diagram in ref. 4. The enthalpy of molten NaOH was also determined at a single temperature, 598 K.

RESULTS

The results are summarized in Fig. 1, which also includes published data for $NaNO_3$ [3] and NaOH [5]. Our value of 8.08 kcal mole^{-1} for NaOH at 598 K, obtained by averaging five results, is extremely close to the line representing the published data, and so, for clarity, is not shown in the Fig.

Relatively few data points were obtained for the solid state, and these seem to fit smooth curves better than straight lines that break abruptly at the melting points. This probably reflects the presence of a small amount of water or carbonate, but slight deviations from the true eutectic compositions may also contribute. Many more measurements were made on the liquid state, with special emphasis on data at $T \simeq 598$ K, a temperature at which $NaNO_3$ and NaOH are also molten. Regression analyses were performed on the results for the liquid state, and the equations so calculated are given in Table 1. As defined in an earlier paper [3], Δh_T is the molar enthalpy referred
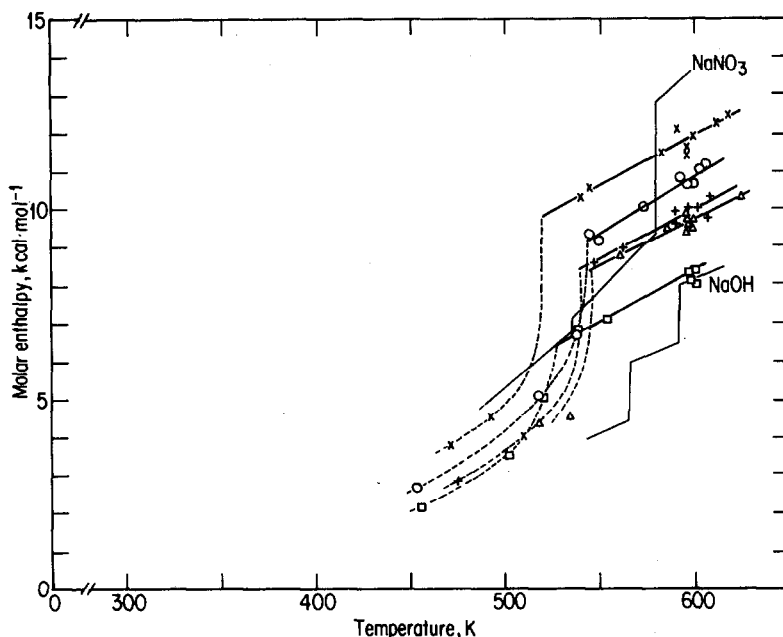
Fig. 1. Experimental data for molar enthalpy as a function of temperature at compositions approximating intermediate compounds and eutectics in the $NaNO_3$–NaOH system. ($NaNO_3$ and NaOH data from refs. 3 and 7, respectively.)×, 0.710 $NaNO_3$·0.290 NaOH; ○, 0.500 $NaNO_3$·0.500 NaOH; +, 0.411 $NaNO_3$·0.589 NaOH; △, 0.327 $NaNO_3$·0.673 NaOH; □, 0.178 $NaNO_3$·0.822 NaOH.

to a temperature that is close to but not at 298 K, the difference between Δh_T and the more usual ($H_T - H_{298}$) being negligibly small in most cases, and the two can be used interchangeably.

TABLE 1

Molar enthalpy as a function of temperature for five solutions in the molten $NaNO_3$–NaOH system

Solution		$\Delta h_T = C_p \times T + b$		Standard deviation (cal mole^{-1})
X_{NaNO_3}	X_{NaOH}	C_p(cal mole^{-1} K^{-1})	b(cal mole^{-1})	
0.710	0.290	25.76	−3540	254
0.500	0.500	30.47	−7430	31
0.411	0.589	26.23	−5760	182
0.327	0.673	24.43	−4960	163
0.178	0.822	26.55	−7550	128

For purposes of energy storage, it is probably most useful to consider and compare the amount of heat stored over a temperature range encompassing the melting temperatures. Values for the range 500–550 K (227–277°C) are

TABLE 2

Heat storage capacity (enthalpy change) at five compositions in the $NaNO_2$–NaOH system over the temperature range 500–550 K

Composition		Enthalpy change, $\Delta h_{550} - \Delta h_{500}$	
X_{NaNO_3}	X_{NaOH}	(kcal mole^{-1})	(cal g^{-1})
0.710	0.290	5.7	79
0.500	0.500	5.2	83
0.411	0.589	5.1	87
0.327	0.673	~5.1	~93
0.178	0.822	3.5	73

given in Table 2. As can be seen, the use of any of these compositions would enable the storage of considerable quantities of heat.

DISCUSSION

The heat of mixing of a binary liquid solution is given by the equation

$$\Delta H_M = (H_T - H_{298})_{sol} - \chi_A(H_T - H_{298})_A^\star - \chi_B(H_T - H_{298})_B^\star \qquad (1)$$

where ΔH_M = molar heat of mixing, χ_A, χ_B = mole fraction of A and B in the solution, and $(H_T - H_{298})_{A \text{ or } B}^\star$ = molar enthalpy of pure A or pure B.

To use the present results to calculate heats of mixing would be somewhat presumptuous; in general, they lack the precision necessary for serious discussion of the implications of the sign or the magnitude. However, at one composition, the measured enthalpy of the solution is sufficiently different from the sum of the molar contributions by the two end members to the enthalpy of the solution that there is no doubt concerning the sign of the heat of mixing.

To avoid attaching numerical values to heats of mixing calculated according to eqn. (1), Δh_{598} has been plotted as a function of mole fraction (Fig. 2). As already mentioned, our average value of 8.08 kcal mole^{-1} for Δh_{598} for

pure NaOH is very close to the published value [5] of 8.128 kcal mole^{-1} for ($H_{598} - H_{298}$). The two therefore appear as a single point. In the case of pure NaNO$_3$, our value for Δh_{598}, determined earlier [3], and ($H_{598} - H_{298}$) calculated from the results of Janz et al. [6] are significantly different, 13.64

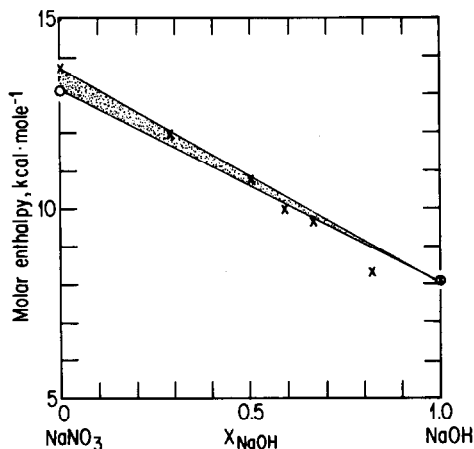Fig. 2. Molar enthalpies as a function of composition at 598 K. ×, Experimental points from this and earlier work [3]; ○, published data by Janz et al. [6] at pure NaNO$_3$ and by Kleppa [7] at pure NaOH.

vs. 13.10 kcal mole^{-1}, and so two points appear. In the event that $\Delta H_M = 0$, a straight line would join the points representing the molar enthalpies of the two pure salts. In Fig. 2, this appears as a wedge-shaped band because of the uncertainty of the enthalpy of NaNO$_3$. At $\chi_{NaOH} \leqslant 0.5$, the enthalpies of the solutions fall within this band, suggesting only very small heats of mixing, whether positive or negative. At $\chi_{NaOH} > 0.5$, all the points fall below the band. At $\chi_{NaOH} = 0.589$ and 0.673, taking into account the experimental uncertainties, it can be concluded only that the heats of mixing are probably negative and probably small. At $\chi_{NaOH} = 0.822$, however, the heat of mixing is indisputably negative, and probably quite large, of the order of -0.7 to 0.8 kcal mole^{-1}; this finding is contrary to the observations of Kleppa [7], who found small positive heats of mixing in solutions of salts with similar charge structures and a common cation.

This unusual behavior, which suggests attractive interactions between the ions, might be attributable to the nature of the anions, namely an oxy-ion and hydroxyl-ion. With this combination, there is the possibility of hydrogen bonding between the OH$^-$ ions and the oxygen atoms of the NO$_3^-$ ions. In this connection, it is interesting to note that the most negative heat of mixing

measured occurs at a composition not far removed from that corresponding to $OH^-/NO_3^- = 3$, i.e. one hydrogen bond to each oxygen atom. Given the small number of compositions studied, this is obviously very speculative, but it can be pointed out that in $HNO_3 \cdot 3 H_2O$, there is a complex system of hydrogen bonds linking NO_3 groups and H_2O molecules in a three-dimensional framework [8]. Such bonds also exist in some basic salts.

The few data available in the literature were obtained solely for heat storage purposes and do not lend themselves well to comparison with the present results. Venkatesetty and LeFrois [1], however, give a specific heat of 23.33 cal mole^{-1} deg^{-1} and a heat of fusion of 2.7 kcal mole^{-1} for 0.7 $NaNO_3 \cdot 0.3$ NaOH compared with 25.76 cal mole^{-1} deg^{-1} and an increase in enthalpy of 5.7 kcal mole^{-1} over $T = 500$–550 K for the closely similar composition (0.710 $NaNO_3 \cdot 0.290$ NaOH) studied in the present work. Considering the small temperature range covered by Venkatesetty and LeFrois (25 K), the specific heat values compare well, but the heat of fusion appears to be lower than would have been obtained in the present work had the composition been exactly that of the eutectic. Cohen and Rice [2] give data for a mixture of 92% NaOH–8% $NaNO_3$ (Thermkeep). Approximately 98 cal g^{-1} can be stored between 516 and 584 K. This high storage capability reflects that this salt mixture is close to pure NaOH in terms of mole fraction of $NaNO_3$ ($\chi_{NaNO_3} = 0.039$). The effect of the addition of nitrate is to depress the melting temperature of the hydroxide to the required level so that the latent heats of the two phase changes in NaOH (fusion at 592 K and solid–solid at 569 K) are both available within the operating temperature of the solar power device under consideration. The low molecular weight of the mixture also benefits the storage capability expressed on a weight basis. No comparison can be made with the present work since no comparable composition was studied.

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