# Cryoscopic Measurements in Fused Salts at Elevated Temperatures

## Preliminary Report

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The calculation of chemical equilibria involving fused salt mixtures at present involves many uncertain assumptions, mainly due to the fact that our knowledge of the thermodynamic properties of fused salts is still very limited. Reliable data on heats of fusion and specific heats in the fused state is scarce, and very little is known about the deviations from ideal solutions of fused salt mixtures.

Kelley and collaborators[1] have carried out very extensive calculations of the heat of fusion of inorganic salts from the phase diagrams. The phase diagrams, however, are for many purposes not sufficiently accurately determined, as they are normally given with rather wide limits of error (more than 2° C). This deficiency becomes particularly clear if one attempts to estimate activity coefficients from the diagrams. Also, there remain unsolved some questions concerning the ionic species present in the salt mixture questions which are of fundamental importance in calculations of chemical equilibria involving fused salts. In the following a method will be described which allows a more precise determination of the liquidus curve of the phase diagram than may be obtained by the usual thermal analysis, thus leading to more accurate thermodynamic data for the fused salts.

The principle of the method is to separate the solid and liquid phases by filtration at the equilibrium temperature and then to determine the composition of the liquid phase after cooling, by chemical analysis. The original idea was taken from a paper by Mason, Hiskey and Ward[2]. They used the principle in their methods of studying the ion distribution equilibria related
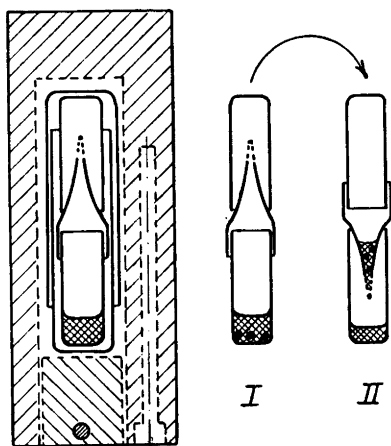
*Fig. 1. Apparatus for high temperature filtration.*

to infra red sensitive phosphors. Our apparatus has a different form as it serves a different purpose (see Fig. 1).

A platinum crucible contains the salt mixture. On top of this crucible is placed an inverted platinum filter, and a second inverted platinum crucible, is placed above the filter.

The salt mixture is kept for a long time at a temperature where solid is in equilibrium with liquid, then the whole arrangement of crucibles and filter is turned upside down by inverting the furnace in which it is placed. Most of the liquid phase then flows through the filter into the second crucible.

The crucibles and filters are placed in a quartz capsule which fits into a solid copper cylinder whose function is to prevent the occurrance of temperature gradients between the thermo-couple, the crucible and the filter. The whole apparatus is placed in an electric furnace, which is swept out with oxygen-free gas to prevent oxidation of the copper cylinder. In order to maintain a constant temperature in the furnace, the electric current is taken from a constant voltage supply. The temperature was measured by means of a Pt-Pt 10 % Rh thermocouple and a compensator from Otto Wolf. The melting point depressions could be measured with an accuracy of 0.1—0.2 ° C and the accuracy of the absolute value of the temperature is estimated to be $\pm$ 0.5°C.

Two systems were investigated —$Na_2SO_4$—$NaCl$ and $Na_2SO_4$-$NaBr$. Only the sulphate side of the phase diagram was determined. The system $Na_2SO_4$-$NaCl$ has been investigated by Jänecke, Wolters[4], Koltchko[5], and the system $Na_2SO_4$-$NaBr$ by Rea[6]. Both are simple eutectics and no solid solution has been found.

The calculation from the phase diagram of the heat of fusion and the deviation from ideal solution do not offer any theoretical problems which have not already been worked out in classical physical chemistry. The formulas used will be briefly reviewed.

The liquidus curve on the sulphate side of the phase diagram gives the composition of the liquid phase which is in equilibrium with solid $Na_2SO_4$. If $f_s$ is the fugacity of solid $Na_2SO_4$, and $f_m$ is the fugacity of $Na_2SO_4$ in the fused mixture, then

$$f_s = f_m$$

Using pure liquid $Na_2SO_4$ as the standard state, the activity of $Na_2SO_4$ in the fused mixture will be

$$a_m = \frac{f_m}{f^0} = \frac{f_s}{f^0}$$

where $f^0$ is the fugacity of pure liquid $Na_2SO_4$.

Further

$$RT \ln a_m = RT \ln \frac{f_s}{f^0} = -\Delta F$$

where $\Delta F$ is the change in free energy on fusing the pure sulphate at a temperature $T$. $\Delta F$ may be expressed in terms of the heat of fusion $\Delta H$ and the temperature. If we neglect the variation with temperature of the heat of fusion, then

$$\Delta F = -RT \ln a_m = \Delta H \left(1 - \frac{T}{T_0}\right)$$

where $T_0$ is the melting point of sodium sulphate.

Introducing $a_m = N_1\gamma_1$ where $N_1$ and $\gamma_1$ are the mole fraction and activity coefficient of $Na_2SO_4$ we obtain

$$\ln N_1 + \ln \gamma_1 = -\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Plotting $\ln N_1$ as a function of $\frac{1}{T}$ should give a straight line in the region where deviations from an ideal solution are small, the heat of fusion being determined by the slope of the line. Deviations from the straight line should give information about the activity coefficients in the mixture.

*Table 1. Corresponding values of the liquidus phase composition and temperature for the systems Na₂SO₄-NaCl and Na₂SO₄-NaBr.*

|  | Temperature °C | $\frac{1}{T}$ 10³ | Molefraction of Na₂SO₄ ($N_1$) in liquid phase | $-\log_{10} N_1$ |
|---|---|---|---|---|
| System Na₂SO₄-NaCl | 857.5 | 0.8844 | 0.9391 | 0.0273 |
|  | 835.3 | 0.9021 | 0.8870 | 0.0521 |
|  | 802.7 | 0.9294 | 0.8185 | 0.0869 |
|  | 683.2 | 1.0455 | 0.5801 | 0.2365 |
| Melting point (extrapolation) | 885.0 |  | 1.0000 |  |
| System Na₂SO₄-NaBr | 843.1 | 0.8958 | 0.9052 | 0.0433 |
|  | 804.9 | 0.9275 | 0.8231 | 0.0845 |

The experimental data are given in Table 1, and Fig. 2 shows $\log_{10} N_1$ as a function of $\frac{1}{T}$ for the systems $Na_2SO_4$-NaCl and $Na_2SO_4$-NaBr. The two systems give practically the same value for the heat of fusion of sodium sulphate. The three points of the system $Na_2SO_4$-NaCl, in which the NaCl content is less than 20 mol%, give 6 040±70 cal/mol for the heat of fusion. The melting point is found by extrapolation to be 885 ° C. Using this melting point, and the two measurements from the system $Na_2SO_4$-NaBr, the heat of fusion is found to be 6 070 cal, thus verifying the value calculated from the system $Na_2SO_4$-NaCl.

The value of the heat of fusion above may be compared with other values found from earlier phase diagram measurements[1, p. 115].

| System | Investigator | |
|---|---|---|
| Na₂SO₄-NaCl | Jänecke | 5 870 |
| » | Klotchko | 5 970 |
| » | Wolters | 5 790 |
| » | Present measurements | 6 040 ± 70 |
| Na₂SO₄-NaBr | »          » | 6 070 |

In these calculations the difference in the specific heats of solid and fused $Na_2SO_4$ is not taken into account as the specific heat of the salt in the liquid state is not known. The difference in the specific heats of the solid and liquid states is of the order of 1 cal/° C for most inorganic salts [1, p. 4]. This will increase the above values of the heat of fusion by about 60 cal, giving *6 100 cal* as the
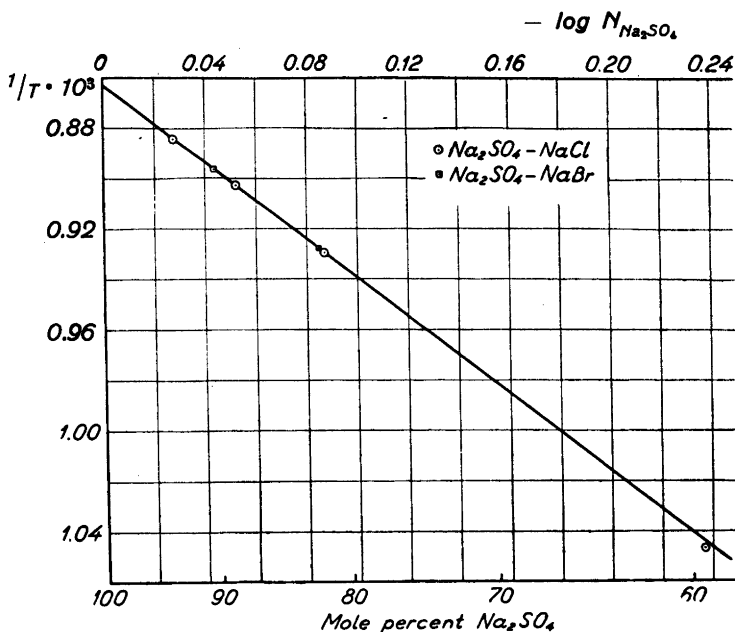
*Fig. 2. The relationship between molefraction of sodium sulphate ($-\log_{10} N_{Na_2SO_4}$) and inverse temperature ($^1/_T$) for the systems $Na_2SO_4$-NaCl and $Na_2SO_4$-NaBr.*

corrected figure. It will also bring the point at about 40 mol% NaCl in Fig. 2 close to the straight line.

Furthermore, measurements in Fig. 2 show that the linear relationship between $\log N_1$ and $\dfrac{1}{T}$ is valid over a very wide interval, indicating that the systems $Na_2SO_4$-NaCl and $Na_2SO_4$-NaBr form ideal mixtures.

## SUMMARY

A method has been worked out which permits an accurate determination of the liquidus curve of phase diagrams at high temperatures. The methode is based on a separation of a fraction of liquid from solid + liquid by filtration at the equilibrium temperature.

The sulphate sides of the binary systems $Na_2SO_4$-NaCl and $Na_2SO_4$-NaBr have been investigated by this method.

From these measurements, the heat of fusion of $Na_2SO_4$ is estimated to be 6 100 cal, and the two systems are found to form ideal mixtures in the liquid state.

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