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On the Phase Diagram
Na_2CO_3—Na_2S

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At STFI a thermodynamic study of reactions in the recovery of spent pulping liquors is in progress. For this investigation a reliable phase diagram for the system $Na_2CO_3 - Na_2S$ was needed. The only earlier studies on this system in the literature seem to be those by Tammann and Oelsen,[1] and by Courtois.[2] The result of the former authors seems to be quite uncertain mainly due to the use of impure Na_2S. Courtois' result is doubtful as his experimental method [3] is unsuitable for two-component systems. Therefore a redetermination seemed necessary and was performed at the Department of Inorganic Chemistry at Umeå University.

The sodium carbonate – sodium sulfide system has been studied mainly by high temperature microscopy (HTM) and differential thermal analysis (DTA).

Experimental. Pure anhydrous Na_2S was prepared as described in Ref. 4. The product was white, analyzed $\geq 99.5 \%$ Na_2S (iodo-

metrically),[5] and had a melting point of $1175°C \pm 10°C$. Na_2CO_3 (May and Baker, *p.a.*) was dried at 500°C under CO_2 and had a melting point of 858°C. All handling, *e.g.*, mixing and weighing of samples, was made in dry N_2 atmosphere in a glove-box.

A Leitz high temperature microscope (HTM) with a 1350 Hot-stage was used. The temperature was measured with a $Pt - Pt(Rh)$ thermocouple. The sample mixture was pressed into a small disc and was then placed between two sapphire plates for direct observation (at $100 \times$ magnification) of melting and solidification processes under a protective atmosphere of N_2. Heating and cooling was done very slowly near the transition temperatures.

The DTA equipment was a Netzsch model 404. The sample and the reference substance (Al_2O_3-powder) were packed in small alumina cups (with graphite lids) placed on the thermocouples. The heating and cooling rate was 5°/min, and was done in an atmosphere of 90 % N_2 and 10 % H_2.

Result and discussion. The results are are shown in Fig. 1. The system has a single eutectic at a mol fraction $Na_2S(x_{Na_2S})$ of 0.40 and at 762°C. Also there is some evidence of solid solubility, at least on the Na_2CO_3 side of the phase diagram. The liquidus temperatures obtained by HTM
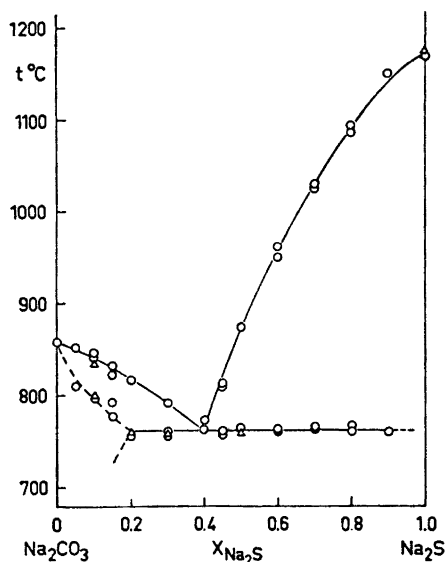

Fig. 1. The phase diagram $Na_2CO_3 - Na_2S$.
O HTM data. △ DTA data.

should be accurate to $\pm 5°$ or better at $x_{Na_2S} < 0.6$, and to about $\pm 10°$ at $x_{Na_2S} > 0.6$. In the DTA work at least two heating and cooling cycles were run in each experiment, but only the heating curves were used for evaluation since supercooling occurred in the cooling cycles.

The transition temperature, *i.e.*, solidus or eutectic, was interpreted as that at which the DTA curve leaves the base line. Eutectic (solidus) temperatures were thus determined to about $\pm 5°$, and as seen in Fig. 1 they were consistent with the HTM data. On the Na_2CO_3 side of the system ($x_{Na_2S} < 0.40$) a continuous peak was usually obtained between the eutectic (solidus) and liquidus temperatures. The liquidus temperature should fall within the decreasing part of the peak on the DTA heating curve, *i.e.*, within $\pm 10°$ in the present study, and this was also found to be consistent with the HTM results.

The solidus temperatures obtained in the range $x_{Na_2S} < 0.2$ indicated a region of solid solubility. We made an attempt to study this further by equilibration of samples ($x_{Na_2S} < 0.2$ or $x_{Na_2S} > 0.85$) in iron capsules at appropriate temperatures followed by quenching to room temperatures within a few seconds. The samples were then directly studied by powder X-ray diffraction with an exposure time of 1/2 h. However, no evidence of a solid solution was found by this method, apparently because Na_2CO_3 reverted to its low temperature modification;[6] thus the initial solid solution probably separated into its constituent components within the time of the quenching or the X-ray study. Because of the uncertainty of the limits of the solid solubility regions they have been indicated by dashed curves in Fig. 1.

One may calculate the activity factor ratio $f(Na_2CO_3(s))/f(Na_2CO_3(l))$ using the

solidus and liquidus data in the range $x_{Na_2S} < 0.40$ and assuming the enthalpy of fusion for Na_2CO_3 to be 7.3 kcal (determined calorimetrically [7-9]). The obtained activity factor ratios range between 1 and 0.9 with x_{Na_2S} between 0.0 and 0.4. The values were found not to be consistent with an ideal or a simple regular model; this is in disagreement with a suggestion in the literature,[10] made on the basis of Courtois' data.[2] Thus, heats of melting for Na_2CO_3 and Na_2S computed using such a model were unreasonably large (*e.g.*, deviated by at least 50 % from the calorimetric value in the case of Na_2CO_3).

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