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The Phase Diagram of the System $SrCl_2$—$BaCl_2$

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The liquidus curve of the system $SrCl_2$ – $BaCl_2$ was determined by thermal analysis and by high-temperature filtration, the solidus by a tracer technique previously described.[3] The system shows complete miscibility in both liquid and solid phases, with a freezing point minimum of 852.0°C at about 68 mole percent $SrCl_2$.

Assuming ideal behaviour of the liquid mixtures, and positive deviations with symmetrical activity coefficients of the type $RT \ln \gamma_A = b N_B^2$ for the solid mixtures, it is shown that with a value of $b \simeq 1$ kcal, a phase diagram can be calculated which gives fairly good agreement with the experimental values.

The binary system $SrCl_2$—$BaCl_2$ was investigated about 45 years ago by Vortisch[1], who also quotes the results of previous workers. More recently, Bergman and Bukhalova[2] checked the earlier results by means of a thermal visual method. According to Vortisch, the system shows complete miscibility in both liquid and solid phases. Our own investigation was aimed particularly at a more precise determination of the solidus curve.

RESULTS AND DISCUSSION

The results are given in Table 1 and in Fig. 1. A comparison between the present and earlier results is given in Table 2. The diagram (Fig. 1) is quite similar to that of Vortisch [1], although in his work, the solidus was largely estimated.

At the strontium chloride side of the diagram, the difference between the solidus and liquidus curves proved to be very small, so small in fact, that the separation of the two curves could not be effected by the present method.

The shape of the phase diagram indicates that the tendency towards forming a solution is weaker in the solid than in the liquid state. Hence the solid solutions will show more positive (or less negative) deviations from ideality than the liquid solutions. The scanty information available regarding the mixing behaviour of molten salt mixtures of the type AX_2 — BX_2 indicates that the deviations from ideality are generally smaller here than in the corre-

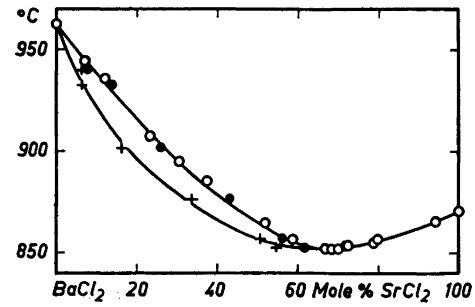

Fig. 1. The system $SrCl_2$ — $BaCl_2$. Open circles: Liquidus points determined by thermal analysis. Filled circles: Liquidus points determined from high-temperature filtration. Crosses: Solidus points determined with ^{134}Cs tracer.

sponding mixtures of the type A'X — B'X. From the phase diagram $CaCl_2$ — $FeCl_2$ it can be concluded that the liquid mixtures in this system show very nearly ideal behaviour.[5] It seems reasonable as a first approximation to assume ideal behaviour for the liquid $BaCl_2$ — $SrCl_2$ mixtures, and interpret the minimum of the liquidus curve as due to positive deviations from ideality in the solid solutions. It is then of interest to see whether the phase diagram can be interpreted by applying simple symmetrical expressions for the activity coefficients of the solid solutions.

A frequently applied set of expressions for the activity coefficients is

$$\begin{aligned} RT \ln \gamma_A &= b\ N_B^2 \\ RT \ln \gamma_B &= b\ N_A^2 \end{aligned} \qquad (1)$$

where γ is the activity coefficient, N the mole fraction and b is a constant. If the entropy of mixing is ideal (*i. e.*, the Sr^{++} and Ba^{++} ions are distributed at random over the cation positions, and the change in vibrational entropy

Table 1. Data of thermal analysis and high temperature filtration of the system $SrCl_2$ — $BaCl_2$.

Thermal analysis		Thermal analysis		High temperature filtration		
Total composition, mole % $SrCl_2$	Temp. of the first crystallization °C	Total composition, mole % $SrCl_2$	Temp. of the first crystallization °C	Equilibrium temperature °C	Composition of phases in equilibrium, mole % $SrCl_2$	
					liquid phase	solid phase
100.0	870.5	58.8	856.6	852.7	61.7	54.9
94.3	865.5	51.9	864.3	857.0	56.3	50.7
79.8	856.7	37.5	884.8	876.5	43.0	34.0
78.8	855.0	70.3	894.8			
72.3	853.7	23.3	907.8	901.8	25.8	16.1
71.9	853.7	12.1	935.6	932.7	13.6	6.5
69.9	852.0	7.1	944.2	940.0	7.6	6.6
68.2	852.0	0.0	962.3			
66.8	852.0					

Table 2. Minimum in the System $SrCl_2$ — $BaCl_2$.

	Temperature °C	Composition mole % $SrCl_2$
Vortisch	845	70
Sandonini	854	65
Bergman and Bukhalova	840	70
This paper	852	68

upon mixing is zero), then b is equal to the partial molar heat of solution of one component in the pure second component.

The equilibrium between solid and liquid phases may be expressed by the well-known equation (valid for both components)

$$\ln a_l - \ln a_s = \frac{\Delta H_m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \quad (2)$$

where the a's are the activities, ΔH_m is the heat of melting, assumed to be independent of temperature (Δc_p for the melting process is neglected) and T_m is the melting point of the pure component. Assuming ideal behaviour of the liquid, eqns. (1) and (2) are combined to give

$$RT \ln N_l/N_s = \Delta H_m\left(\frac{T}{T_m} - 1\right) + b\,(1 - N_s)^2 \quad (3)$$

which is also valid for both components. The heats of melting for $SrCl_2$ and $BaCl_2$ are taken as 4.1 and 5.4 kcal/mole, respectively, as estimated by Kelley[6] from phase diagrams.

The experimental data do not fit this equation too well, since the best-fit value of b differs for the two sides of the diagram; a value of about 1.2 kcal is found for the $SrCl_2$ side, 0.6 kcal for the $BaCl_2$. The uncertainty in these b-values is rather large, however, and application of the symmetrical equation (3) with a value of $b = 1.0$ kcal may be equally reasonable. Fig. 2 shows that this gives a phase diagram quite similar to the experimental (minimum at 847°C and 71 mole percent $SrCl_2$). The differences between calculated and

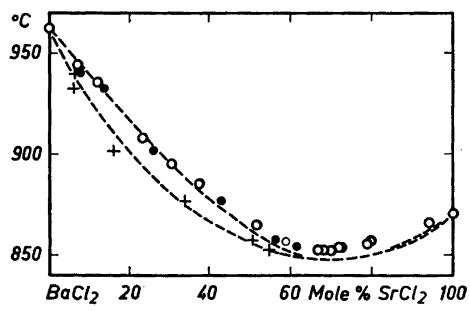

Fig. 2. The system $SrCl_2$ — $BaCl_2$. Dashed lines calculated (see text). Experimental points, same as in Fig. 1, shown for comparison.

experimental values seems not to be outside the possible errors caused by the approximations involved in eqn. (2) and by the probably inaccurate values for the heats of fusion.

EXPERIMENTAL

The liquidus of the system was determined by ordinary thermal analysis. A Pt/90 Pt 10 Rh thermocouple, with the bare leads dipping into the molten salt, was used for temperature measurement. The thermocouple was checked against the melting point of pure NaCl (800.4°C).

The solidus was determined by a method developed by Seltveit and Flood[3]. The principle is as follows: To a mixture of known composition within the system is added a small amount (*e.g.*, 0.05 %) of a radioactive third component which is soluble in the liquid, but insoluble in the solid phase of the system. The mixture is heated to complete fusion and the specific activity of this liquid is determined. Next, the mixture is cooled to a temperature where liquid and solid phases are coexistent, and kept at this temperature until equilibrium is established (usually overnight). A small sample of the liquid is then filtered off and its composition determined by chemical analysis. This analytical composition serves as a check on the liquidus obtained from thermal analysis. On another sample of the liquid, the specific activity is determined. From the increase in tracer content per gram of liquid (as compared to the content when the whole system was fused) the weight-ratio of liquid to solid can be determined, and thus the solidus.

The chemicals used were $BaCl_2$ *p.a.* and $SrCl_2$ *puriss. cryst.* (both from Merck A.G.) dried at 150°C. As tracer component was used $CsCl_2$ with a content of ^{134}Cs (half life 2.3 years) obtained from JENER, Lilleström, Norway. The assumption that the Cs^+ ion cannot enter the solid solutions of $SrCl_2$ — $BaCl_2$ was not proved by experiment. But it is known from previous work[3] that NaCl does not enter into solid solution in the $CaCl_2$ lattice, and the radius ratio r_{Cs+}/r_{Ba++} is more unfavourable than the ratio r_{Na+}/r_{Ca++} with respect to solid solution formation.

The salt mixtures were analyzed by conventional methods[4]. Barium was precipitated by an excess of potassium dichromate, and after filtration the excess of chromate was titrated with sodium thiosulphate. Strontium was taken as difference. As an extra check, the chloride content was determined by titration with silver nitrate, using chromate as indicator (after removal of barium by sulphate addition). The tracer activity was determined by an EKCO Scintillation Counter N 550.

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REFERENCES

1. Vortisch, E. *Neues Jahrb. Mineral., Geol. Beilage* **38** (1914) 185.
2. Bergman, A. G. and Bukhalova, G. A. *J. Gen. Chem. USSR* **19** (1949) 553.
3. Seltveit, A. and Flood, H. *Acta Chem. Scand.* **12** (1958) 1030.
4. Scott, W. W. *Standard Methods of Chemical Analysis* Vol. I, 5th Ed. D. Van Nostrand Company, New York 1939, p. 128 and 272.
5. Flood, H., Cyvin, S. J. and Solli, O. *Unpublished work.*
6. Kelley, K. K. *Bureau of Mines, Bull.* **393** (1936) p. 20 and 117.

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