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The System $CaSiO_3$-CaF_2

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The phase diagram of the system $CaSiO_3$—CaF_2 has been determined. From the depression of the freezing point it could be shown that, in the molten form, calcium metasilicate is polymerized by the condensation of three SiO_3^{2-} units probably in the form of a ring structure. Further, the activities of the components have been determined. The curves of the activity coefficients show some very interesting features.

The system $CaSiO_3$—CaF_2 has previously been studied by Karandéeff [1] and to a lesser extent by Tursky [2]. The former used the method of thermal analysis and found the system to be a simple one with eutectic point at 48 mole-% and 1 130° C (Fig. 1, dotted lines). The main difficulty was the undercooling at the silicate-rich side of the diagram. It is to be noticed, however, that recent determinations have given much higher melting points for the pure components. Tursky studied only a few melts in the microscope furnace and did not get satisfactory results due to reactions in the melts.

The present work utilizes the method of electric conductivity. In silicate-rich systems, this method will give no satisfactory results but, in CaF_2-rich mixtures, it is possible to obtain good values for the liquidus curve since CaF_2 is a crystallizer. The technique has been described in an earlier investigation [3] on the system CaO—CaF_2, from which the melting point of the fluoride, quoted below, has been taken. The melting point of pure $CaSiO_3$ is taken from the system CaO—SiO_2 [4]. It should be mentioned that no significant loss of fluoride occurs if the components of the mixtures are ignited and cooled before mixing, whereas 3—7 % will be lost when melting is performed without first driving off moisture.

The results have been recorded in Fig. 1. Dotted lines are from Karandéeff. The eutectic point was found at 41 mole-% $CaSiO_3$ and 1 127° C.

From measurements of the heat content of pure CaF_2, Naylor [5] has determined the heat of fusion, L_f = 7 100 cal/mole, and the heat capacities of the liquid and solid states. If we put the value for L_f into the expression for the freezing point depression together with the melting points of CaF_2 and CaF_2-

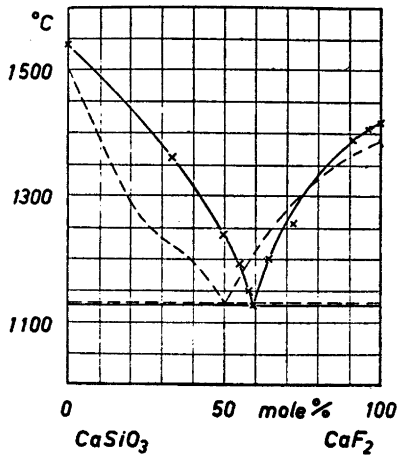

Fig. 1

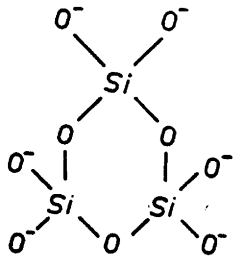

Fig. 2

rich mixtures, the mole fraction of solute can be computed. It is found that these values are only about one third of those given in Table 1, column 2. This indicates the association of three silicate units SiO_3^{2-}, *i. e.* the formula for the dissolved calcium metasilicate is $Ca_3Si_3O_9$. From X-ray investigations [6] it is known that crystallized calcium metasilicate, wollastonite, has a ring structure of just three SiO_3 units (Fig. 2). Probably this ring structure is also maintained in the pseudowollastonite existing above 1 150° C as well as in the molten state. This configuration has earlier been suggested by Bockris and Lowe [7] during the course of determinations of viscosities in molten Ca-silicates. They explain (see also Kozakevitch [8]) the decrease in viscosity of Ca-silicates, caused by addition of CaF_2, as a depolymerization action of the fluoride but from our results above such an explanation cannot be possible.

Taking into account the difference in molar heat of the solid and fused CaF_2, or ΔC_P, the activity of calcium fluoride in the melt can be computed using the formula

$$-\ln a_{CaF_2} = \frac{L_f \cdot \Delta T}{R \cdot T \cdot T_o} + \frac{\Delta C_P}{R}\left(\ln\frac{T_o}{T} + 1 - \frac{T}{T_o}\right)$$

Table 1.

Melting point °K	From weighing		Computed from freezing point depression		Apparent degree of polymerisation
	Mole fraction $CaSiO_3$	Mole $CaSiO_3$ per CaF_2	Mole fraction of solute	Mole solute per CaF_2	
1 691	0.000	0.0000	0.0000	0.0000	
1 680	0.040	0.0416	0.0137	0.0139	2.99
1 663	0.091	0.1000	0.0349	0.0362	2.76

Table 2.

Melting point °K	$x_{Ca_2Si_2O_6}$	x_{CaF_2}	$-\ln a_{CaF_2}$	a_{CaF_2}	$-\ln f_{CaF_2}$	f_{CaF_2}
1 691	0.000	1.000	0.000	1.000	0.000	1.000
1 680	0.0137	0.986	0.0138	0.986	0.000	1.000
1 663	0.0325	0.968	0.0356	0.965	0.0025	0.998
1 530	0.115	0.885	0.243	0.784	0.121	0.887
1 474	0.158	0.842	0.342	0.710	0.170	0.843
1 400	0.188	0.812	0.498	0.608	0.290	0.749

The results are summarized in Table 2. The composition will now be more adequately described by the mole fractions $x_{Ca_2Si_2O_6}$ and x_{CaF_2}, which are given in columns 2 and 3. The last two columns give the activity coefficients, $f = a/x$.

The activity coefficients can be expressed by the formula $-\ln f_{CaF_2} = 7.79 \cdot x^2_{Ca_2Si_2O_6}$, which using the Gibbs-Duhem formula yields $\ln f_{Ca_2Si_2O_6} = 15.58 \cdot x_{Ca_2Si_2O_6} - 7.79 \cdot x^2_{Ca_2Si_2O_6}$. Both activity coefficients are then put equal to unity in pure CaF^2, *i. e.* very dilute calcium silicate. For the eutectic mixture, where $x_{Ca_2Si_2O_6} = 0.188$, the values will be $-\ln f_{CaF_2} = 0.275$, $f_{CaF_2} = 0.759$ and $a_{CaF_2} = 0.617$ and also $\ln f_{Ca_2Si_2O_6} = 2.654$, $f_{Ca_2Si_2O_6} = 14.20$ and $a_{Ca_2Si_2O_6} = 2.67$.

We now consider the silicate-rich side of the diagram and need to know the heat of fusion for $Ca_3Si_3O_9$. This value can be computed from the system calcium metasilicate and diopside [9]. In this system $\ln x_{Ca_2Si_2O_6}$ turns out to be, within the experimental error, a linear function of $1/T$. This shows the liquid to be very nearly an ideal solution, and the heat of fusion for $Ca_3Si_3O_9$ comes out to be 40 800 cal/mole. As we do not know the heat capacities of solid and liquid silicate at the temperatures in question, we must disregard ΔC_p. There might be some solubility of Mg-silicate in the pseudowollastonite but Shairer and Bowen [9] consider it to be rather small. It is believed that the error in L_f arising in this way will have increased the value by at most two or three percent.

We now obtain the activity values summarized in Table 3. It is a strange coincidence that the activity coefficient for the silicate has very nearly the same value in the eutectic melt as in the pure silicate liquid.

Table 3.

Melting point °K	$x_{Ca_2Si_2O_6}$	x_{CaF_2}	$-\ln a_{Ca_2Si_2O_6}$	$a_{Ca_2Si_2O_6}$	$-\ln f_{Ca_2Si_2O_6}$	$f_{Ca_2Si_2O_6}$
1 813	1.000	0.000	0.000	1.000	0.000	1.000
1 633	0.403	0.597	0.624	0.536	0.287	1.333
1 513	0.250	0.750	1.122	0.326	0.265	1.304
1 466	0.214	0.786	1.338	0.263	0.206	1.229
1 423	0.195	0.805	1.550	0.212	0.083	1.087
1 400	0.188	0.812	1.669	0.189	0.003	1.003

Table 4.

Melting point °K	$x_{Ca_3Si_3O_9}$	x_{CaF_2}	$f_{Ca_3Si_3O_9}$	f_{CaF_2}
1 813	1.000	0.000	1.000	1.400
1 631	0.400	0.600	1.330	0.704
1 602	0.350	0.650	1.356	0.696
1 564	0.300	0.700	1.354	0.697
1 513	0.250	0.750	1.303	0.706
1 434	0.200	0.800	1.122	0.739
1 400	0.188	0.812	1.003	0.759
1 491	0.150	0.850	0.614	0.839
1 580	0.100	0.900	0.310	0.925
1 646	0.050	0.950	0.151	0.981
1 691	0.000	1.000	0.071	1.000

In computing the activity of the silicate in Table 3, we have used the pure substance as standard state, but in the formula for ln $f_{Ca_3Si_3O_9}$ above, we used the very dilute solution. The formula is renormalized giving $f = 1$ for pure silicate by substracting 2.65, which changes the value for the eutectic mixture 2.654 (see above) into 0.003 (Table 3). The values of f_{CaF_2} on the silicate side of the eutectic point are obtained by numerical integration of Gibbs-Duhem equation. The results are summarized in Table 4 and Fig. 3.

Here we can see that the activity coefficient of $Ca_3Si_3O_9$ rises to a maximum at about 33 mole-% and then decreases to a rather low value. It is interesting to notice that at the maximum there are two molecules of fluoride to one molecule of silicate.

In a pure silicate melt the divalent calcium ions will bind together the big *cyclo*-trisilicate ions by strong electrostatic forces and we suggest that this

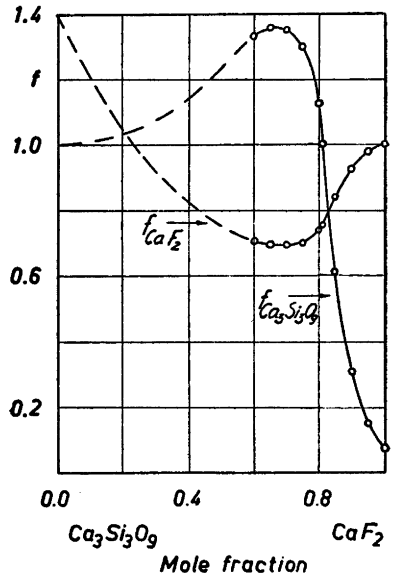

Fig. 3

is the cause of the high viscosity found by Herty *et al.*[10] and by Bockris and Lowe [7]. If we add calcium fluoride, the electrostatic binding will be broken because CaF^+ ion pairs are added to the large anions. We consider this to be the cause of the lower viscosity in the mixtures [10], but we find the substitution of O by F in the silicate ions, which has been proposed by other authors (*e. g.*[7,8]), to be rather improbable. Such a solvatization *e. g.* $Ca_3Si_3O_6 \cdot 3CaF_2$ will also explain the low activity coefficient of $Ca_3Si_3O_9$ diluted in CaF_2 and the low activity of CaF_2 in the same melts. In concentrated solutions with less CaF_2, the activity effects found might be explained by the stretching of the electrostatic bindings of the divalent Ca^{++} ions to the silicate ions by the added F^- ions and the corresponding compressing effect on the calcium fluoride.

REFERENCES

1. Karandéef, B. *Z. anorg. Chem.* **68** (1910) 188.
2. Tursky, F. *Z. anorg. Chem.* **82** (1913) 315.
3. Bååk, T. *Acta Chem. Scand.* **8** (1954) 1727.
4. Bowen, N. L., Schairer, J. F. and Posnjak, E. *Am. J. Sci.* **26** (1933) 193.
5. Naylor, B. F. *J. Am. Chem. Soc.* **67** (1945) 150.
6. Barnick, M. *Diss.* Berlin 1936.
7. Bockris, J. O' M. and Lowe, D. C. *Proc. Royal Soc. London* A **226** (1954) 431.
8. Kozakevitch, P. *Rev. Mét.* **51** (1954) 581.
9. Schairer, J. F. and Bowen, N. L. *Am. J. Sci.* **240** (1942) 730.
10. Herty, C. H., Hartgren, F. A. and Jones, G. T. *Mining Met. Invest. U.S. Bur. Mines, Carnegie Inst. Technol. and Mining Met. Advisory Boards, Coop. Bull.* **50** (1931).

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