A thermodynamic analysis of the system anorthite–åkermanite.

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Summary. From thermodynamic considerations of the system anorthite–åkermanite it appears that the melts in this system are ionic in nature. The liquidus relation in this system would thus seem to afford confirmation of the theory, based on conductivity measurements, that silicate melts such as molten anorthite dissociate into such ions as Ca^{2+} and $(Al_2Si_2O_8)^{2-}$.

Further thermodynamic calculations involving no unreasonable assumption lead to a close reproduction of the experimental liquidus curve of åkermanite. This lends added strength to the belief in the stable existence of åkermanite down to the eutectic; no evidence in support of the claim that åkermanite becomes unstable below 1 325° C. (Osborn and Schairer, 1941) was encountered.

According to Osborn *et al.* (1954) the presence of substantial Ca^{2+} increases the desulphurizing potential of blast furnace slag. The thermodynamic treatment of the binary system anorthite–åkermanite leads to the conclusion that both phases dissociate in the molten state and in mutual solution to yield Ca^{2+}; it therefore appears probable that a high concentration of these minerals in the slag would have a salutary effect on the slag chemistry.

THE system anorthite–åkermanite is a binary system located in the petrologically and technologically significant four component system $CaO–MgO–Al_2O_3–SiO_2$. Experimentally this system has already been investigated (de Wys and Foster, 1956) as has the ternary system anorthite–åkermanite–diopside of which it is a join (de Wys and Foster, 1958). The location of these systems in the basic four-oxide system is indicated in fig. 1. This figure indicates the position of the ternary system in the tetrahedron; a hollow, transparent tetrahedron has been used to permit a clearer view of the plane under consideration.

Technologically, some of the industrial glasses, cements, and virtually all usual iron blast-furnace slags are included in the lime–magnesia–alumina–silica system, according to McCaffery *et al.* (1927), Koch (1933), Osborn *et al.* (1954), and Prince (1951). Since apparently the properties of slag are not mere composites of the properties of SiO_2, Al_2O_3, MgO,

and CaO, but rather of the mineral compounds present, an investigation of the interrelationships of some of the minerals should be useful. According to Martin and Derge (1943) a knowledge of possible liquid
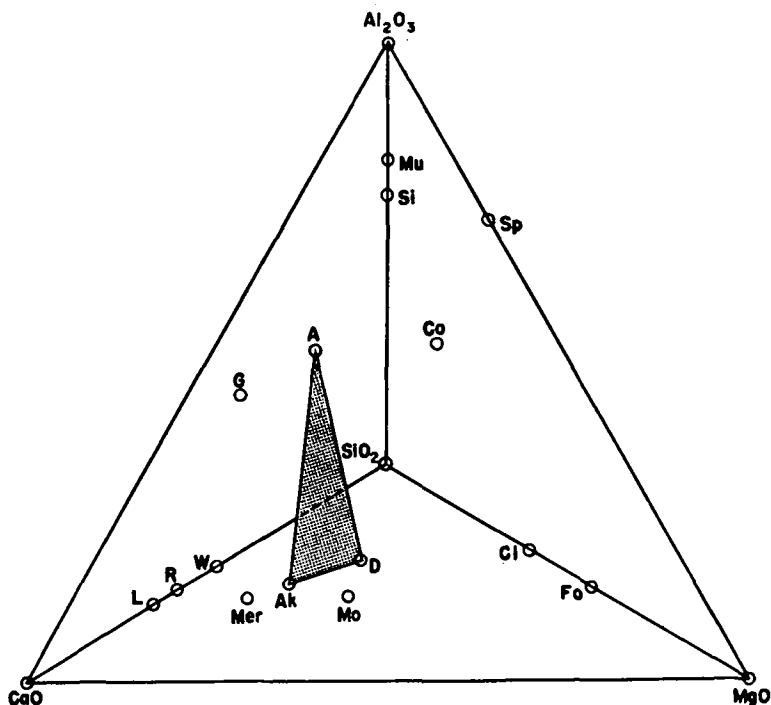

FIG. 1. The lime–magnesia–alumina–silica tetrahedron. The shaded area represents the anorthite–åkermanite–diopside ternary plane. The abbreviations have the following significance: A, anorthite; D, diopside; Ak, åkermanite; Mu, mullite; Si, sillimanite; Sp, spinel; Co, cordierite; G, gehlenite; L, larnite; R, rankinite; W, wollastonite; Mer, merwinite; Mo, monticellite; Fo, forsterite; Cl, clinoenstatite.

structural units in the slag would greatly clarify the nature of the chemical reactions in such a fluid, and would help to explain reactions between mineralogical melts and metal. Such knowledge would facilitate a greater control of slag chemistry. Accordingly, a thermodynamic analysis of the system anorthite–åkermanite was undertaken in an attempt to formulate possible structural units present in silicate melts of this type.

Thermodynamic discussion and results. Experimentally it has been established that the freezing-point depression of a melt depends both on the

nature of the solvent and on the degree of dissociation or association of the solute. Assuming an ideal solution, an equation relating these two factors to each other follows directly from the Clausius–Clapeyron equation. The equation may be expressed as follows: $\Delta T_f = RT_0T/\Delta H_f i \ln N_1$ where ΔT_f is the freezing-point depression of the solution, T_0 is the melting-point of the primary phase, T is the liquidus temperature of the primary phase region, ΔH_f is the latent heat of fusion of this phase, R is the gas constant in calories per mole, N_1 is the mole fraction of the solvent. i is the so called van't Hoff factor which may be defined as the ratio of the effect produced by a mole fraction of an electrolyte to the effect observed for an equal mole fraction of non-electrolyte. If $i = 1$, the solution is non-electrolytic.

By and large, a two-component system may be considered practically ideal if the molecular volumes of the components are nearly equal (Wagner, 1952). Therefore, since the molecular volumes of anorthite and åkermanite are about 100·6 and 93·3 respectively, assuming the density of anorthite as 2·765 (Morey, 1954) and of åkermanite 2·922 (Ervin and Osborn, 1949), it would appear that such a system may be considered ideal compared for example to a system involving either of the above phases with diopside, which has a molecular volume of about 66·3.

The above equation was therefore utilized for the calculation of a theoretical diagram for the system anorthite–åkermanite with a view to comparing experimental and calculated liquidus curves. Since the ΔH_f ranges of values for anorthite and åkermanite have been published (Goranson, 1942) and the T_0 for these compounds are well known it is possible to calculate ΔT_f ranges for any selected value of the mole fraction of either component acting as a solvent and for various i factors.

Fig. 2 shows two calculated liquidus zones. The upper zone is the result calculated with an i factor of 1, while the lower zone shows the result of a calculation with an i factor of 2. Since the lower calculated zone shows an excellent correlation with the experimental curve, it is reasonable to conclude that an i factor of 2 is more applicable to this system. The i factor of 2 may be taken as a strong indication that the silicate melt is electrolytic in nature. Such a conclusion appears to be quite conservative in that it agrees with numerous authors such as Doelter (1907 and 1908), Farup *et al.* (1924), Martin and Derge (1943), Bockris *et al.* (1948), and Barth and Rosenquist (1949). All of the above observed that the numerous silicate melts with which they were concerned did act as strong electrolytes.

The foregoing treatment permits the construction of a tentative model of the anorthite–åkermanite silicate melt. Darken and Gurry (1953), Bockris *et al.* (1948), Barth and Rosenquist (1949), and others, believe that the essential difference between solid and molten silicate lies in the
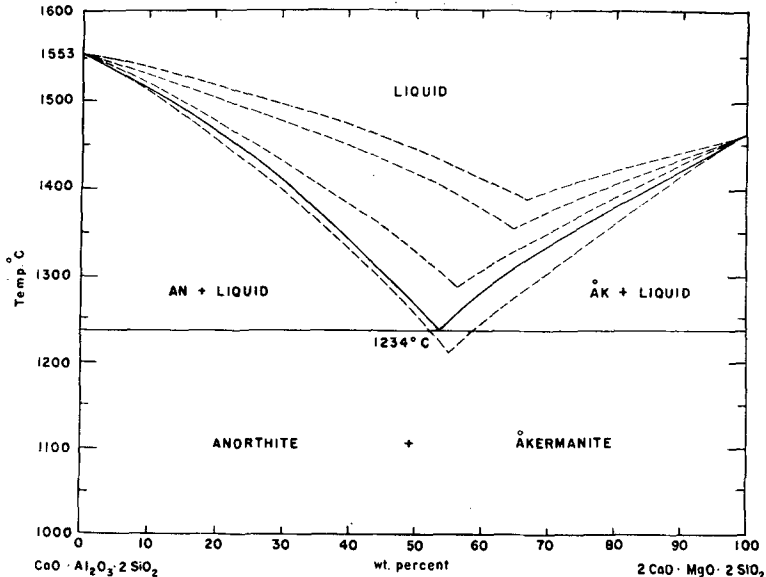

FIG. 2. Comparison of theoretical and experimental liquidus curves for the system anorthite–åkermanite. Upper zone lying between the dashed lines is the calculated liquidus zone on the basis of a ΔH_f value for anorthite ranging from 375 to 505 J/g. and a ΔH_f value for åkermanite between 315 and 445 J/g., and an i factor of 1. The lower liquidus zone, lying between the lower pair of dashed lines represents the results of freezing point lowering calculations with similar ΔH_f values and an i factor of 2. Note that the experimental curve (solid line) falls within the lower liquidus zone.

degree of order or disorder. According to this point of view the liquid state is characterized by an extended network lacking symmetry and periodicity. Bockris *et al.* consider the molten silicates as consisting of irregularly arranged silicate rings and chains with cations in the interstices. Martin and Derge in experimenting with liquids of anorthite compositions indicate that at 1 450° C. calcium migrated to the cathode while a complex alumina silicate moved to the anode. They concluded, therefore, that in the molten slag such a composition is present as Ca^{++} and a complex silico-aluminate ion. Blau (1951) indicated that in

super-cooled silicate melts there are two distinct types of oxygen ions. He divided them into those that bridge two 'network-forming' cations, and those that are connected to only one 'network-forming' cation and have valence charges balanced by the considerably more loosely held and distant 'network-modifying' cations. Blau then apparently indicates that when the ratio 'network-forming' cations to oxygen is $1:2$ all the oxygens in the silicate melt are bridging. This agrees with tables by Evans (1952) concerning similar ratios in silicate structures. Blau proceeds to provide further ratios and their connexion to the types of oxygen present. A melt of anorthite has definitely a ratio of $1:2$ and thus such a liquid would tend to have all bridging oxygens. A complex $(Al_2Si_2O_8)^{--}$ as well as Ca^{++} would therefore result from such an ionic melt. Such a point of view would then agree with the observations by Martin and Derge. Also, such dissociation of the dissolved anorthite into ions of that type would explain an i factor of 2 for the åkermanite liquidus curve. In general the åkermanite composition would tend to classify it among the sorosilicates. Eitel (1952) prefers to classify åkermanite among the phyllosilicates; he indicates that the Si_2O_7 groups are combined with (MgO_4) tetrahedra to form fivefold annular structures, complexes of the composition $(Mg_2Si_4O_{14})^{8-}$. The i factor of åkermanite electrolyte would then be $2\frac{1}{2}$. Considering Blau's calculation and looking upon Mg as a network former from his point of view, the ratio would be 0.428. This would allow such a composition to fall into the category of 3 to 4 bridging oxygens per tetrahedron of (SiO_4) or (MgO_4). According to Evans such a ratio would be classified as a sheet structure.

The fact that an i factor of 2 appears to fit the experimental curve while structural considerations tend to indicate a factor of $2\frac{1}{2}$ might be due to incomplete dissociation of the units.

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