

electron donor is the main contributing factor to the rate-determining step in these inner sphere reactions.

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CHEMISTRY

Crystalline Solution in $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ on the Join $\text{Ca}_3\text{Al}_2\text{O}_6$ - $\text{Ca}_3\text{Fe}_2\text{O}_6$

THE extent of substitution of ferric iron for aluminium in tricalcium aluminate has been investigated using conventional high-temperature phase equilibrium techniques. Starting materials were mechanical mixtures of reagent-grade oxides. Raw mixtures were suspended for several hours in platinum-foil envelopes at the hot spot of a platinum-wound vertical-tube resistance furnace. Temperatures were read using a Pt-90Pt10Rh thermocouple frequently calibrated against melting points defined on the 1948 International Temperature Scale. Identification of phases in the quenched products was made by use of X-ray diffraction and of transmitted-light microscope.

A condensed phase equilibrium diagram for a portion of the join $\text{Ca}_3\text{Al}_2\text{O}_6$ - $\text{Ca}_3\text{Fe}_2\text{O}_6$ through the system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ is shown in Fig. 1. The maximum extent of the field of tricalcium aluminate crystalline solutions was found to be 3.5 moles per cent ' $\text{Ca}_3\text{Fe}_2\text{O}_6$ ' at 1,389° C, the temperature of the ternary invariant point. At this temperature, a tricalcium aluminate crystalline solution of composition $\text{Ca}_3\text{Al}_{1.93}\text{Fe}_{0.07}\text{O}_6$ co-exists with liquid, lime, and a calcium alumino-ferrite phase of

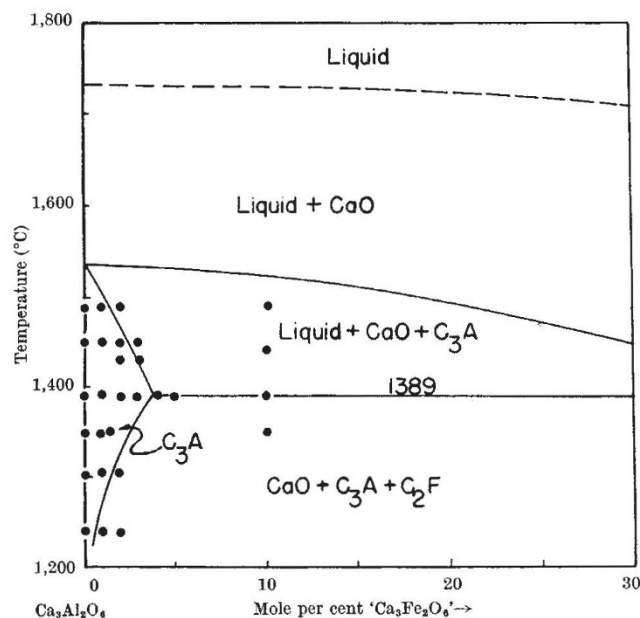


Fig. 1. Condensed phase equilibrium diagram for a portion of the join $\text{Ca}_3\text{Al}_2\text{O}_6$ - $\text{Ca}_3\text{Fe}_2\text{O}_6$ through the system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. Liquidus data inferred. $\text{C}_3\text{A} = \text{Ca}_3\text{Al}_2\text{O}_6$ crystalline solution, $\text{C}_2\text{F} = \text{Ca}_2\text{FeO}_5$ - $\text{Ca}_2\text{Al}_2\text{O}_5$ crystalline solution.

composition $\text{Ca}_2\text{Al}_{1.08}\text{Fe}_{0.92}\text{O}_5$. Other phase relations determined in this investigation were in good agreement with the results of Newkirk and Thwaite¹.

The possibility of reduction of some iron in these mixtures to the ferrous state was investigated by wet chemical techniques developed by Ingamells². Analysis of samples on the join $\text{Ca}_3\text{Al}_2\text{O}_6$ - $\text{Ca}_3\text{Fe}_2\text{O}_6$, which had been heated to liquidus temperatures and quenched, showed less than 0.25 per cent of the total iron to be in the ferrous state. These results show that reduction of ferric iron is not a significant factor in equilibrium relations in this portion of the system $\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$. Consequently, loss of ferrous iron to platinum containers in runs made at liquidus temperatures is not extensive enough to influence appreciably experimental results in this type of investigation.

Careful determination of tricalcium aluminate lattice constants as a function of iron content showed only very minor variations from the values for the pure end member.

These equilibrium relationships are of considerable importance to the understanding of the behaviour of Portland cement clinker, of which both tricalcium aluminate and dicalcium ferrite crystalline solutions are important constituents. If tricalcium aluminate in cement clinker contains substantial amounts of iron, as suggested by the results of the work recorded here, then the distribution of iron and aluminium among clinker phases, and the factors controlling this distribution, will be more complicated than previously realized. Calculation of mineralogical content of cement clinker, as by the Bogue method, should be based on realistic crystalline solution compositions and not on simplified end members.

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Mechanism of Crystal Growth for the Enzyme Chymotrypsinogen

IN a previous publication¹ it was shown that the morphology of chymotrypsinogen crystals was dependent on the supersaturation at which they were formed. Particular emphasis was laid on the nucleation mechanism. In the following work evidence is presented which suggests the underlying mechanism of the enzyme crystallization.

Low supersaturation. At low degrees of supersaturation the enzyme crystallizes from aqueous solution at room temperature as hollow whiskers as shown previously. One possible explanation for this type of growth is that the individual molecules are aligned in the crystalline product in a stereoregular manner. If the crystal could grow by a screw dislocation mechanism, then the material near the axis of the screw would be highly strained. In certain unfavourable cases the strain energy may be so great that the crystal grows with the molecules avoiding the core area and hence forming hollow tubes. With such a mechanism the molecules may be aligned around the tube in a configuration similar to that shown in Fig. 1. Thickening of the tubular growth could ensue by deposition of subsequent layers in a similar configuration. In support of the foregoing assertions we have found tubular chymotrypsinogen crystals wound into a macroscopic spiral configuration. These spirals show strong birefringence under polarized light, indicating an aligned structure (Fig. 2). The growth of these tubes is usually very slow, thus providing time for winding of the molecules into the regular array.