874. *High-temperature Studies of the System Calcium Oxide–Phosphorus Pentoxide.*

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A revised phase diagram of the partial system $2CaO,P_2O_5$–CaO is presented, incorporating a new phase field for $\bar{\alpha}$-$3CaO,P_2O_5$ and a region of solid solution between $3CaO,P_2O_5$ and $2CaO,P_2O_5$.

Portions of the system $CaO–P_2O_5$ have been studied by several previous workers with differing conclusions.[1,2] Interest in the larger system $CaO–P_2O_5–SiO_2$ prompted us to reinvestigate the partial system $2CaO,P_2O_5$–CaO concerning which there is controversy in the literature. Furthermore, we have recently discovered a new form of tricalcium phosphate,[3,4] and revision of previous phase diagrams is thus needed.

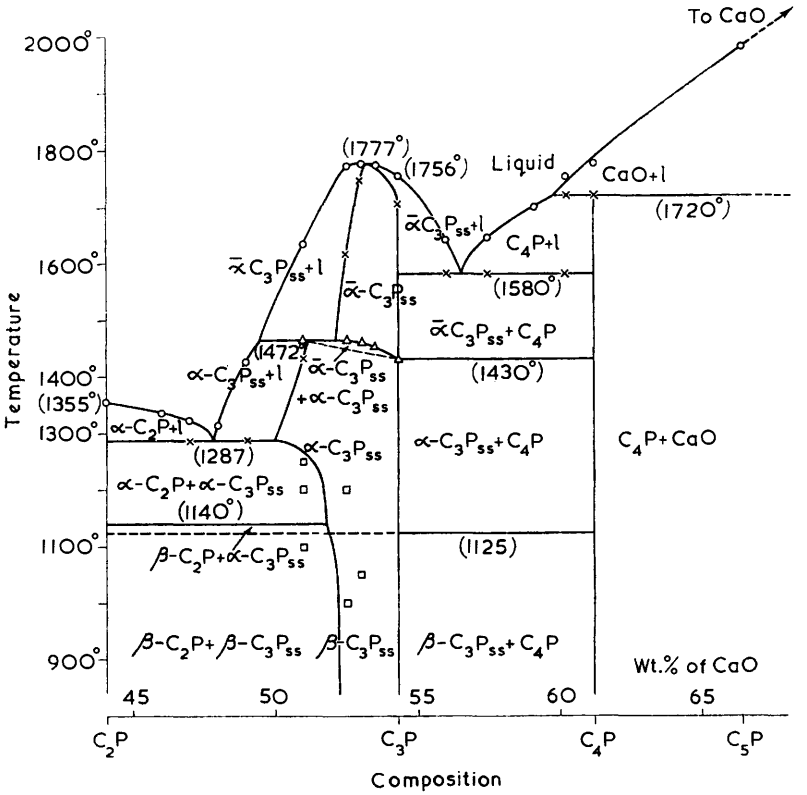
Experimental.—The preparation of materials and experimental procedure were as described earlier,[4] except for the following. Volatilization of phosphorus pentoxide from substances varying in compositions between $2CaO,P_2O_5$ and $3CaO,P_2O_5$, and of calcium oxide from those between $3CaO,P_2O_5$ and $4CaO,P_2O_5$ precluded the use of high-temperature *X*-ray analysis which requires prolonged heating of the specimen. Much of the system was explored by high-temperature microscopy, which is sufficiently rapid to avoid this difficulty, but for phase identification in the subsolidus region the traditional quenching method followed by *X*-ray analysis in a Guinier-type focusing camera was also used. Selective " free lime " analysis [5] was used to investigate the possibility of solid solution between $4CaO,P_2O_5$ and CaO.

Results and Discussion.—The new phase diagram is presented in the Figure and affirms by direct observation the congruent melting of $2CaO,P_2O_5$ (1355° c) and the incongruent melting of $4CaO,P_2O_5$ (1720°). In disagreement with earlier work [1] the liquidus curve reaches a maximum, not at $3CaO,P_2O_5$ (1756°), but very near the composition $53CaO,47P_2O_5$ (weight %) (1777°), and there is limited miscibility between $2CaO,P_2O_5$ and $3CaO,P_2O_5$. It has been established by 'free lime" analysis of compositions richer in lime than

[1] Trömel, *Stahl und Eisen*, 1932, **52**, 396; Trömel, *Mitt. Kaiser Wilhelm Inst. Eisenforsch.*, 1932, **14**, 25; Korber and Trömel, *Z. Elektrochem.*, 1932, **38**, 589; Korber and Trömel, *Arch. Eisenhüttenw.*, 1933, **1**, 7; Bredig, Franck, and Füldner, *Z. Elektrochem.*, 1932, **38**, 158; Bredig, Franck, and Füldner, *Z. Elektrochem.*, 1933, **39**, 959; Trömel, *Stahl und Eisen*, 1943, **63**, 21.
[2] Trömel, Harkort, and Hotop, *Z. anorg. Chem.*, 1948, **256**, 253.
[3] Nurse, Welch, and Gutt, *Nature*, 1958, **182**, 1230.
[4] Nurse, Welch, and Gutt, *J.*, 1959, 1077.
[5] Lerch and Bogue, *Ind. Eng. Chem., Analyt.*, 1930, **2**, 296.

$4CaO,P_2O_5$ that there is no solid solution between CaO and $4CaO,P_2O_5$; and no optical or *X*-ray evidence of solid solution between $4CaO,P_2O_5$ and $3CaO,P_2O_5$ was found.

High-temperature microscopy was successful in determining the course of the $\alpha \longrightarrow \bar{\alpha}$ inversion of $3CaO,P_2O_5$, the temperature of which rose with increasing solid solution of $2CaO,P_2O_5$. This technique did not reveal the $\alpha \longrightarrow \beta$ inversions of either $2CaO,P_2O_5$ or $3CaO,P_2O_5$, which were detected by quenching and *X*-ray analysis. Evidence that the quenching procedure was not wholly satisfactory was obtained from the observed presence



The system $2CaO,P_2O_5$–CaO.

O, Liquidus temperature. △, Temperature of $\alpha \longrightarrow \bar{\alpha}$ transition of C_3P_{ss} by optical examination. ×, Temperature of initial liquid formation. □ Points at which determinations were made with the focusing *X*-ray Guinier camera on quenched specimens. – – – – Broken lines indicate inferred boundary curves.

C = CaO, P = P_2O_5, l = liquid, ss = solid solution.

Temperatures are according to the International temperature scale of 1927.

of three phases, α-$2CaO,P_2O_5$, β-$3CaO,P_2O_5$, and α-$3CaO,P_2O_5$ in the composition $51CaO,49P_2O_5$ (weight %) after quenching from 1200° or 1250°. Presence of β-$3CaO,P_2O_5$ after quenching from a temperature above the inversion $\beta \longrightarrow \alpha$-$3CaO,P_2O_5$ which occurs at 1125° in pure $3CaO,P_2O_5$ (ref. 4) suggests the failure of quenching to preserve α-$3CaO,P_2O_5$. Although the $\alpha \longrightarrow \beta$-$3CaO,P_2O_5$ inversion in the pure compound takes place sufficiently slowly to be arrested easily by quenching, it appears that the presence of α-$2CaO,P_2O_5$ solid solution catalyses the inversion.

Precise location of the $\alpha \longrightarrow \beta$ inversions in $2CaO,P_2O_5$ and $3CaO,P_2O_5$ for mixtures lying between these compositions was not attempted, and the phase diagram shows boundaries projected at an assumed constant temperature from the inversion temperatures

determined for the pure compounds. For this purpose the $\alpha \longrightarrow \beta$ inversion of $3CaO,P_2O_5$ at 1125° was taken from our earlier work [4] and the $\alpha \longrightarrow \beta$ inversion of $2CaO,P_2O_5$ at 1140° is that reported by Hill, Faust, and Reynolds.[6] We have not investigated the low-temperature (−40° and +35°) inversions in $3CaO,P_2O_5$ noted by Koelmans, Engelsman, and Admiraal.[7]

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[6] Hill, Faust, and Reynolds, *Amer. J. Sci.*, 1944, **242**, 458.
[7] Koelmans, Engelsman, and Admiraal, *J. Phys. and Chem. Solids*, 1959, **11**, 172.