Thermodynamics study of CaF$_2$ containing melts.

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Abstract
The isothermal phase relations for the Al$_2$O$_3$-CaF$_2$-SiO$_2$ and CaF$_2$-CaO-P$_2$O$_5$ systems were investigated at 1673 K and 1623 K, respectively, and their liquidus was evaluated by a combination of the hot-filament and the chemical equilibrium techniques. Activity of P$_2$O$_5$ in CaF$_2$-CaO-P$_2$O$_5$ melt was also determined under controlled atmosphere. The hot-filament technique was preferable for observation of the congruent transformation temperature of transparent specimens. The phase relation of a system including a two liquid state was discussed.

INTRODUCTION

Calcium fluoride is a convenient additive to enhance the fluidity of the flux in hot metal pre-treatment. It decreases the melting point of the mixture of calcium oxide and silicates and increases the reactivity. However, reduction in the emission of fluoride is also mandatory because of its negative environmental impact. The concentration of fluorine in wastewater is restricted to within 0.8mg/l in Japan. The volatile species of high temperature liquid flux may result in pollution of the environment, and the disposal of after-use slag may result in fluoride which seeps into the earth. The objective of this study was to decrease the use of fluoride in steelmaking and thus minimize its impact on the environment.

The following processes are effective in reducing fluoride:
(1) Use of another additive that can retain the same reactivity of the flux as a substitute for calcium fluoride.
(2) Separation and recycling of fluoride from afteruse slag.
(3) Minimization of the amount of slag formed in the hot metal pre-treatment process.

Aluminum oxide may be a candidate as a calcium fluoride substitute. Although a phase diagram for the Al_2O_3-CaF_2-SiO_2 system has been reported, it is restricted to the region of two liquid phases: sa is well known, some oxyfluoride systems such as CaF_2-SiO_2 systems have a two liquid phase state.

A miscibility gap might be exploited to separate the oxide rich and fluoride rich phases. Little is yet known of the phase relation required to develop a separation process of fluoride from afteruse slag and a subsequent recycling process. The liquidus saturated with SiO_2 and the region of a homogeneous liquid and a miscibility gap in the Al_2O_3-CaF_2-SiO_2 system were studied to learn whether substituting Al_2O_3 for CaF_2 is possible.

A CaO-CaF_2 based flux is used to remove phosphorus in molten steel, and in order to minimize the slag volume the concentration of phosphorus must be raised. Thermodynamic data available on high P_2O_5 content slags is insufficient, so the CaF_2-CaO-P_2O_5 system was investigated as a basic system for such slags.

EXPERIMENTAL

The phase relations for the Al_2O_3-CaF_2-SiO_2 and CaF_2-CaO-P_2O_5 systems were determined using both a quench chemical analysis and a hot-filament technique. The activity of P_2O_5 for the CaF_2-CaO-P_2O_5 system was measured by the former equilibrium technique.

Quench Chemical Analysis Technique
Phase relations
The solid oxide phase was equilibrated with the liquid phase in a controlled atmosphere. Liquidus saturated with SiO_2 in the Al_2O_3-CaF_2-SiO_2 system and those with CaO, $4CaO \cdot P_2O_5$ and $CaF_2 \cdot 3Ca_3(PO_4)$ in the CaF_2-CaO-P_2O_5 system were measured.

Measurements were made by SiC electric resistance furnace connected to a controller with a Pt-6%Rh/Pt-30%Rh thermocouple. The temperature was controlled within $\pm$1K over a length of 40 mm in a mullite tube (outside diameter: 60 mm, inside diameter: 52 mm, length:600 mm) in the furnace.

Silica and graphite crucibles were used as containers under Ar and carbon saturated carbon monoxide atmosphere, respectively. These held 2 grams of a Al_2O_3-CaF_2-SiO_2 or CaF_2-CaO-$3CaO \cdot P_2O_5$ mixture with a 0.5 gram pellet of saturating oxide. The crucible with the specimen was equilibrated for 1 h at 1673K or 6 h at 1623K. Saturating oxide pellets were prepared by sintering the Al_2O_3-SiO_2 or CaO-$3CaO \cdot P_2O_5$ mixture at 1673K for 12h. The formation of compounds was confirmed by X-ray analysis.

After the specimens were withdrawn from the furnace, they were quenched by flushing with

Ar gas and the fluxes were separated from the saturating oxide pieces. The composition of flux was determined by analyzing the Al, Ca and P content using inductively coupled plasma (ICP-AES) emission spectrometry, the Si content by using a gravimetric technique and O content by using a simultaneous nitrogen and oxygen determinator (LECO).

Activity of P_2O_5 in the slag

Distribution of phosphorus between flux and silver was measured, one gram of silver and of CaF_2-CaO-P_2O_5 flux were equilibrated in a graphite crucible. The atmosphere was controlled with carbon monoxide and a carbon crucible. The activity of P_2O_5 was calculated from phosphorus content in silver, the Gibbs energy change of dissolution of phosphorus into silver, and partial pressure of the oxygen set for the experiment. The phosphorus content in silver was determined by the ICP-AES method.

The activity of P_2O_5 for the CaF_2-CaO-P_2O_5 flux in C/CO atmosphere at 1623K was derived as follows.

The dissolution of phosphorus into silver alloys and its Gibbs energy change are expressed as eqs. 1 and 2,

$$\frac{1}{2}P_2(g) = \underline{P}(mass\%)_{inAg} \tag{1}$$

$$\Delta G = -20.5 + 0.35T \quad J/mol \,^{1)} \tag{2}$$

$$P_{P_2}^{1/2} = \frac{f_P \cdot [mass\%P]}{K} \tag{3}$$

where K is the equilibrium constant of eq.1, and fp is the activity coefficient of phosphorus in Ag relative to 1 mass% in pure Ag. The activity coefficient can be unity because the concentration of P and other elements in Ag was small enough. The partial pressure of P_2 was determined by the concentration of P in Ag as eq.3.

Using phosphorus partial pressure, the activity of P_2O_5 for CaF_2-CaO-P_2O_5 flux can be obtained as follows:

The formation of P_2O_5 is expressed as eq. 4.

$$P_2(g) + \frac{5}{2}O_2(g) = P_2O_5(l) \tag{4}$$

$$\Delta G^\circ = -1{,}580{,}000 + 506 \quad J/mol \,^{2)} \tag{5}$$

Oxygen partial pressure was controlled by atmosphere, therefore the activity of P_2O_5 is fixed as eq. 6.

$$a_{P_2O_5} = \frac{P_{P_2} \cdot P_{O_2}^{5/2}}{K} \tag{6}$$

Where aP_2O_5 is the activity referenced to pure liquid P_2O_5.

Hot-Filament Technique

The hot-filament technique was used to measure the temperature of phase transformation: the liquidus and the congruent transformation point of two liquid phases. Details of the technique are described elsewhere.[3,4] A 0.5mm diameter Pt-6%Rh/Pt- 30%Rh thermocouple was used as a heating device, as holder of the sample, and also to measure temperature.(Fig.1) The temperature was calibrated by measuring the known melting points of KBr, NaCl, K₂SO4, and $12CaO \cdot 7Al_2O_3$.

Two grams of reagent grade SiO_2, CaF_2, and Al_2O_3, or CaF_2, CaO and $3CaO \cdot P_2O_5$ were carefully weighed and thoroughly mixed in an agate mortar. About 10 mg of the mixture was set on the tip of a filament (junction of the thermocouple) and was melted and quenched in advance.

The hot-filament cell was purged with argon gas to eliminate water vapor; the gas was

introduced at a flow rate of 50ml/min. Temperature of the sample during the measurement was increased by about 30K per minute, and the measurement was completed within 90 s. The difference between composition of the mixture and that after melting was less than ±1mass% as confirmed by chemical analysis. The specimen was observed visually by a microscope with a video camera placed above the hot-filament cell. Phase transformation was observed as the temperature of the filament and specimen increased.

A solid phase melted completely at the liquidus temperature. Two liquids mixed into one at the congruent transformation point, two-liquid phases mixing into one-liquid phase. A ripple was observed when the two liquids become one; it appeared inside a drop of the sample at the congruent transformation. The ripple disappeared immediately with increase in temperature. Temperatures were observed simultaneously at the phase transformation. The variation in temperature change was less than 2 degrees during the period of observation.

RESULTS AND DISCUSSION

The Al_2O_3-CaF_2-SiO_2 System

The miscibility gap is shown in Fig.2. The isothermal congruent transformation points at 1673, 1698 and 1723K are represented as lines, and the dashed curves represent the miscibility gap reported by Hillert[5]. These lines exhibit good agreement. The results are restricted to within the region where the isothermal lines run parallel to tie lines in the two-liquid phase area. The congruent temperature decreased with increasing Al_2O_3 concentration.

Phase relations for the Al_2O_3-CaF_2-SiO_2 system are shown in Fig. 3, and the liquidus saturated with SiO_2 was measured by chemical equilibrium technique. SiO_2 and $3Al_2O_3 \cdot 2SiO_2$ were doubly saturated at 20mass% Al_2O_3. A phase diagram for the Al_2O_3-CaF_2-SiO_2 system at 1673K is proposed as in Fig. 3.

The liquidus saturated with SiO_2 crosses the boundary of the immiscibility. Therefore, four regions exist as shown in Fig. 3: I is one liquid, II is one liquid saturated with SiO_2, III is two liquids saturated with SiO_2, and IV is two liquids. This indicates that the two liquid phases equilibrated with SiO_2 are separated into fluoride rich liquid and oxygen rich liquid. The CaF_2-SiO_2 system can be a diagonal phase diagram of CaF_2-CaO-SiF_4-SiO_2. Existence of a three-phase region indicates that the two liquid phases in the CaF_2-SiO_2 system are actually separated into a fluoride rich liquid phase and an oxide rich liquid phase. The maximum solubility of SiO_2 to liquid phase in the Al_2O_3-CaF_2-SiO_2 system at 1673K increases from 40 to 55 mass% with increase in the Al_2O_3/ CaF_2 ratio from 0 to 1.

The CaF_2-CaO-P_2O_5 System

The phase relation at 1623K

Figure 4 shows the isothermal phase relation for the CaF_2-CaO-P_2O_5 system at 1623K. Liquidus saturated with CaO, $4CaO \cdot P_2O_5$ and $CaF_2 \cdot 3Ca(P_2O_5)_3$ were measured by the chemical equilibrium technique. Because the loss of fluoride by evaporation could not be ignored, this slag-metal chemical equilibrium technique could not be applied for measuring liquidus saturated with CaF_2.

There is a liquid phase over the 4 mass% P_2O_5 region with a ratio of about 80/20 CaF_2/CaO. Maximum solubility of CaO is 53.7 mass% at liquidus doubly saturated with CaO-$4CaO \cdot P_2O_5$.

Activity of P_2O_5

Figure 5 shows the composition of liquidus and the activity of P_2O_5 in the flux on liquidus in carbon saturated carbon monoxide atmosphere.

The activity of P_2O_5 increases with increasing P_2O_5 concentration, but do not change noticeably with change in CaF_2/CaO ratio.

Activity of P_2O_5 at CaO and $4CaO \cdot P_2O_5$ doubly saturated is 6.15×10^{-23}.

CONCLUSION

Phase relations for Al_2O_3-CaF_2-SiO_2 and CaF_2-CaO-P_2O_5 systems were investigated by the hot-filament and chemical equilibrium technique at 1673 and 1623K, respectively, and the following conclusions drawn:

(1) Two liquids and SiO_2 phases coexisted in the high SiO_2 and low Al_2O_3 regions.

(2) The miscibility gap disappeared with the addition of more than 15 mass % of Al_2O_3 to the CaF_2-SiO_2 system at 1673K.

(3) Substitution of a small amount of Al_2O_3 for CaF_2 increased the solubility of SiO_2 in Al_2O_3-CaF_2-SiO_2 melt. Partial substitution of Al_2O_3 for CaF_2 in slag enlarged the region of liquid phase. Al_2O_3 might be adequate substitute for CaF_2.

(4) Solubility of CaO increased with increasing P_2O_5 concentration in the CaF_2-CaO-P_2O_5 system.

(5) Because of the strong affinity between CaO and P_2O_5, the activity of P_2O_5 is low on the liquidus saturated with CaO.

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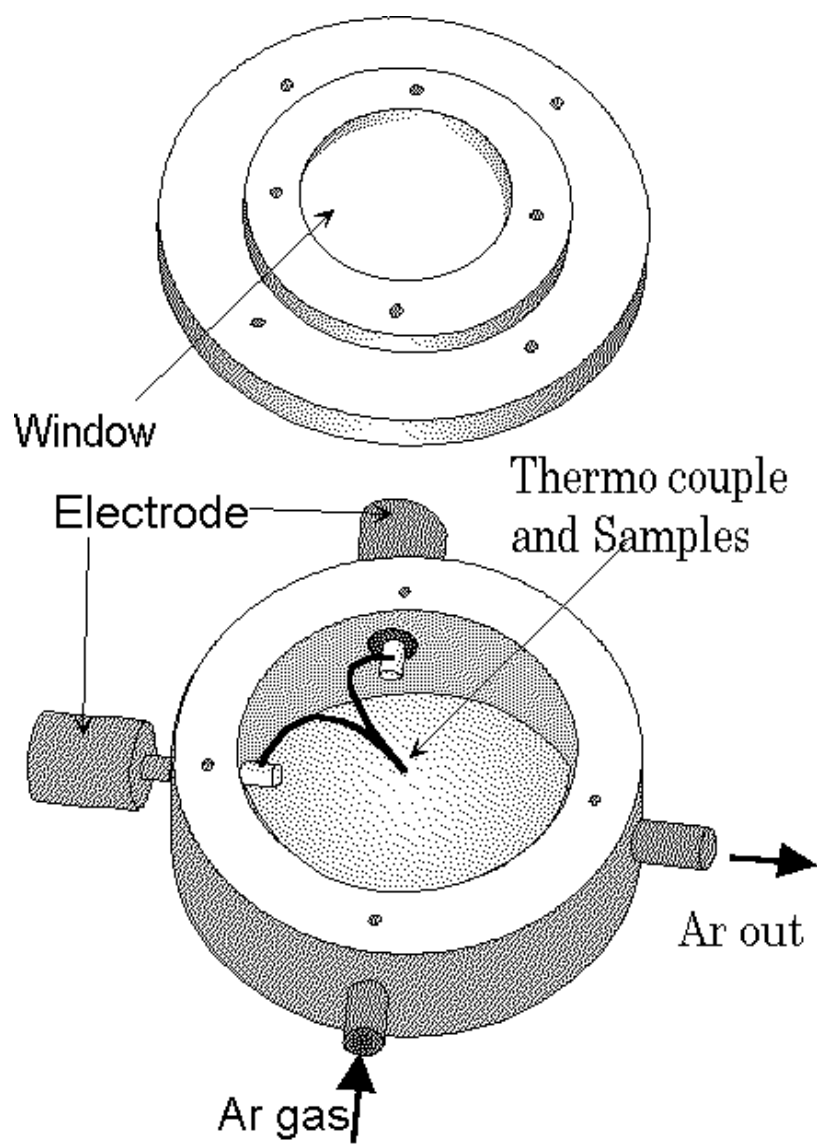5. L.H.Hillert, Acta Polytech. Scand., Chemistry Including Metallurgy, Series No.90, 1970.

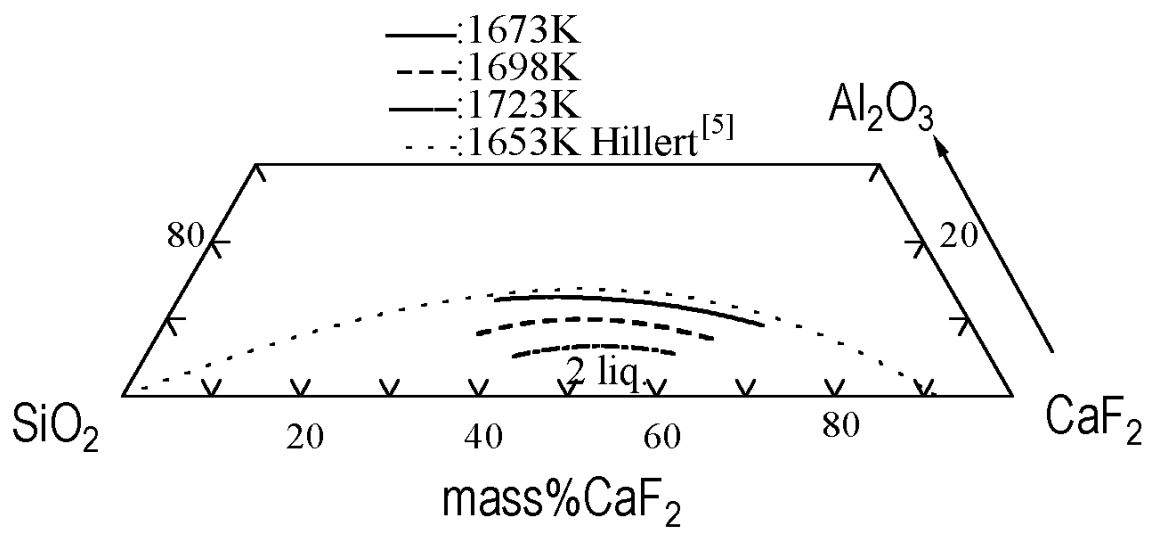Figure 1: Schematic sketch of Hot-filament cell.

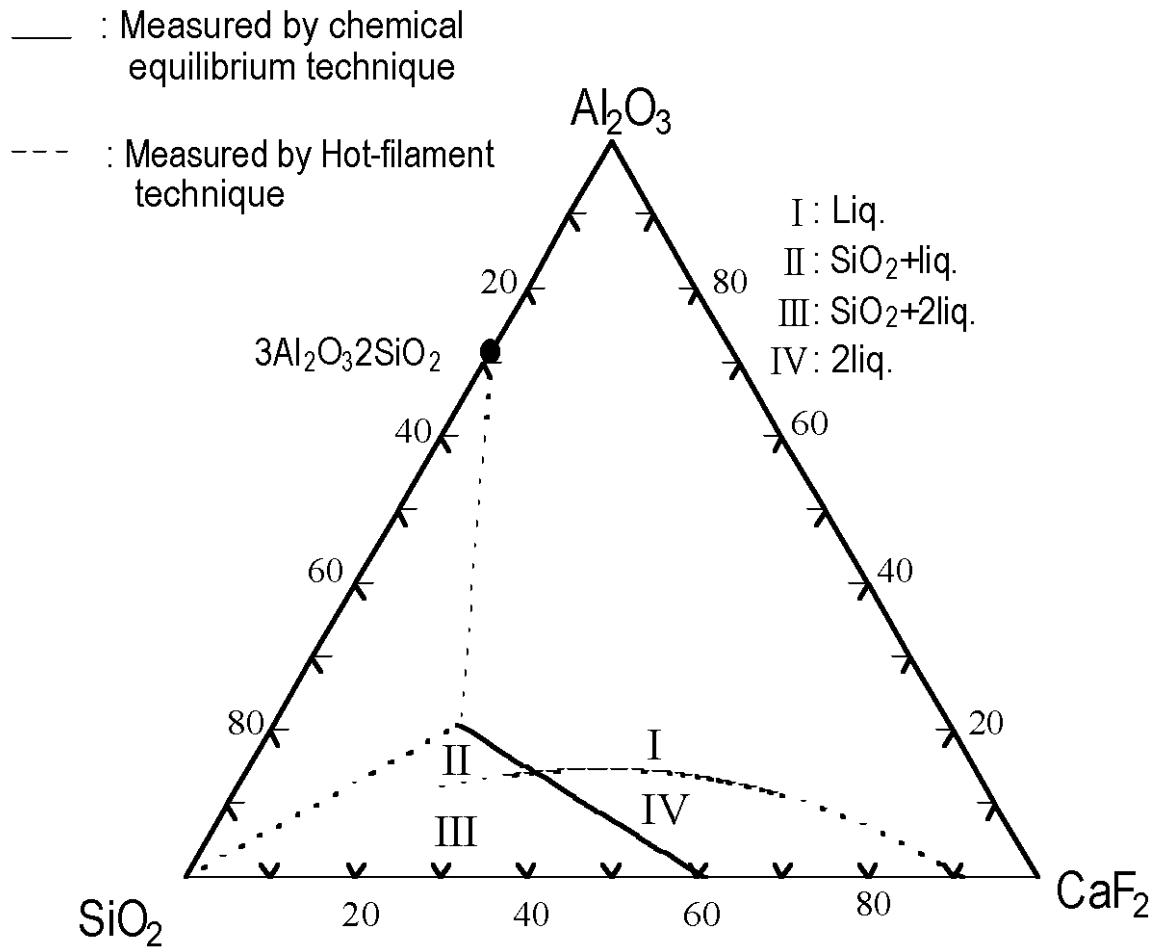Figure 2: Two-liquid region of the Al_2O_3-CaF_2-SiO_2 system.
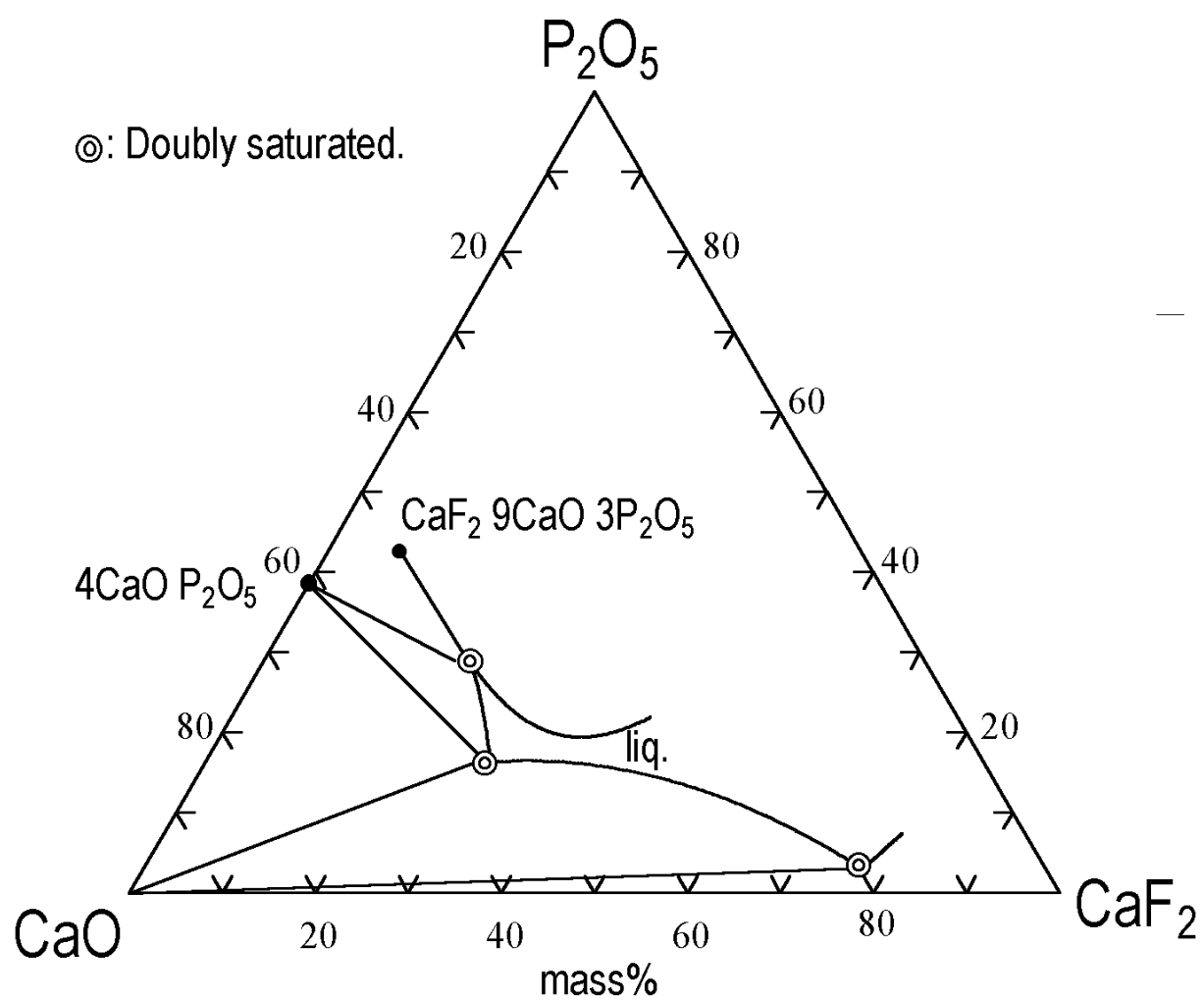
Figure 3: Phase relation of the Al_2O_3-CaF_2-SiO_2 system.
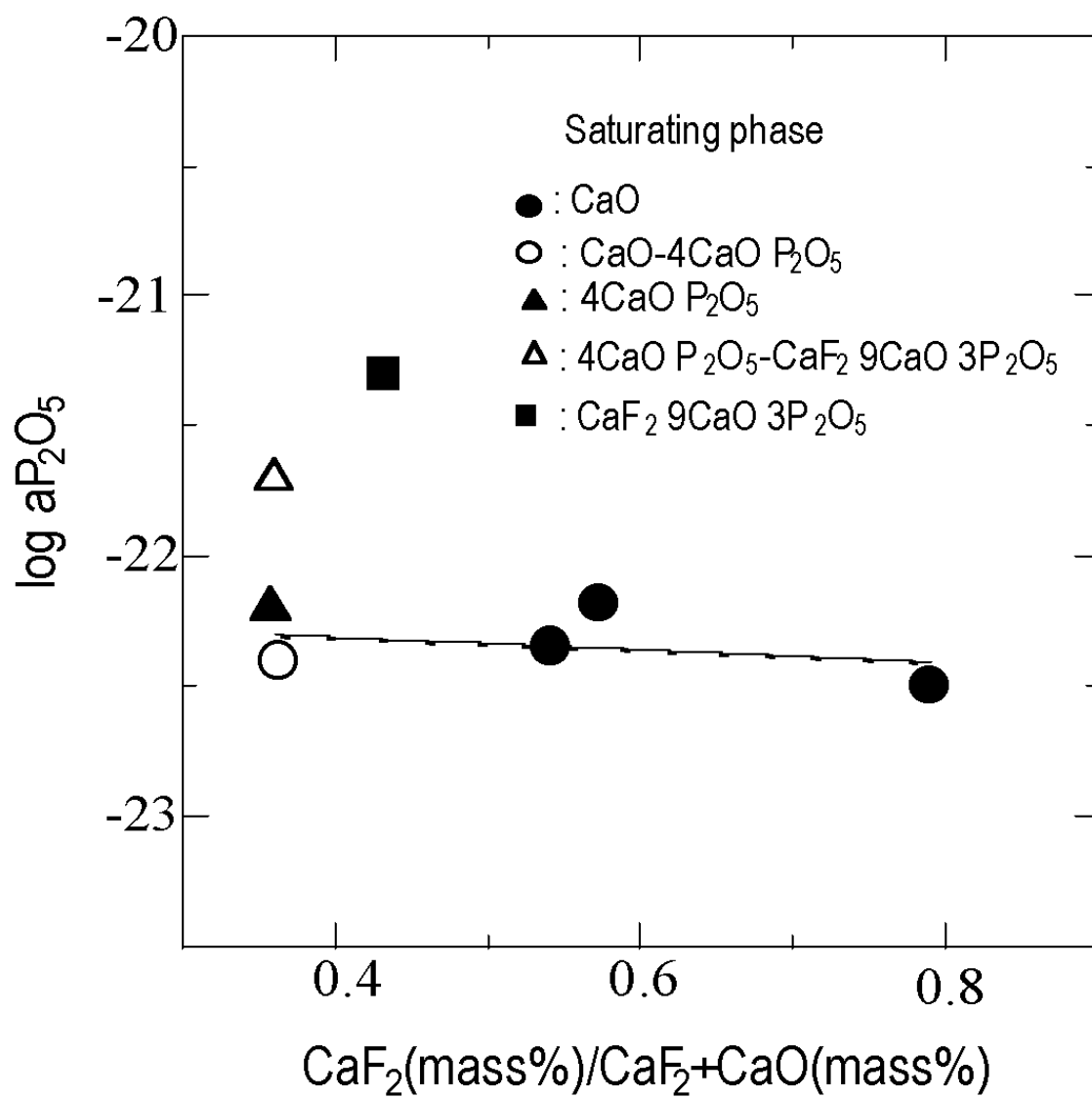
Figure 4: Phase relations for the CaF_2-CaO-P_2O_5 system.

Figure 5: Activity of P_2O_5 on liquidus at 1623K.