

# STRUCTURE RELAXATION OF SILICATE MELTS CONTAINING IRON OXIDE

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## **Abstract**

The changes of oxidation states and coordination structures of iron ions in calcium-silicate melts during the equilibration process have been determined by Mössbauer spectroscopy. The fraction of  $\text{Fe}^{3+}$  ions to the total iron ions became constant within 2h after the equilibration operation was started. On the other hand, it took 20 and 6h for the coordination structures of  $\text{Fe}^{3+}$  ions to settle down by sharing between tetrahedral and octahedral sites when the samples were melted at 1608 and 1678K, respectively. It has been found that the structural coordination of the melts is determined by rearrangement of oxygen ions.

## Introduction

Production of new methods of slag recycling is a significant problem in iron and steel making industry. To solve the problem, it is necessary to consider not only the slag composition but also the state of ions that the slag is composed of, because the state of ions is relevant to the physicochemical properties of slag. As for steel making slag, it is important to investigate the oxidation states and the coordination structures of iron ions.

Many investigators have studied the state of iron ions in silicate glasses using optical absorption(1-3), Mössbauer spectroscopy(4-15), x-ray absorption near-edge structure (XANES)(3) and extended x-ray absorption fine structure(EXAFS) measurements(3,12,16,17). In silicate glasses containing iron oxides prepared in air, it has been reported commonly that  $\text{Fe}^{2+}$  ions act as network modifier, resulting in octahedral coordination. However, there has been no agreement obtained about the coordination of  $\text{Fe}^{3+}$  ions among previous investigations. This is because  $\text{Fe}^{3+}$  ions have two possibilities of being tetrahedrally and octahedrally coordinated and the melting condition of silicates such as temperature and partial pressure of oxygen affect the coordination structure. Accordingly, the coordination structure of  $\text{Fe}^{3+}$  ions in silicate melts should be determined and discussed in consideration of the 'equilibration' of the melts with the melting condition.

The attainment to equilibrium of silicate melts containing iron oxides has been conventionally judged from the experimental result that the fraction of  $\text{Fe}^{3+}$  (or  $\text{Fe}^{2+}$ ) ions to the total iron ions reached a constant value. In addition, the coordination structure of  $\text{Fe}^{3+}$  ions is also affected by the melting condition and should be used as an index to judge the attainment to equilibrium. To the best of our knowledge, however, there are no reports that focus on both the oxidation states and the coordination structures of iron ions to judge the attainment to equilibrium. Consequently, the aim of this study is to observe relaxation of the oxidation states and the coordination structures of  $\text{Fe}^{3+}$  ions in calcium-silicate melts during the equilibration process using Mössbauer spectroscopy.

## Experimental

A master glass of 40(mol%)CaO-40SiO<sub>2</sub>-20Fe<sub>2</sub>O<sub>3</sub> was prepared from reagent grade SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> powders, the last being decomposed to CaO by heating at 1473K for 24h. Powders of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were dried at elevated temperatures. The reagents were weighed to the desired composition and mixed in a mullite mortar. About 30g of the mixture was melted in a platinum crucible at 1773K for 2h in air or melted at 1773K for 10h in a flow of CO-CO<sub>2</sub> mixture ( $P_{\text{O}_2}=5.3 \times 10^{-6}$  atm). Glassy samples were prepared by pouring the melts onto a water-cooled copper plate in air and then crushing. In order to monitor the relaxation of the state of iron ions, about 150mg of samples were melted again at temperatures of 1608, 1678, 1773 and 1858K for 2 – 72h in platinum crucibles (5mm in outer diameter, 0.1mm in wall thickness and 15mm in height) in air and then quenched into water. To confirm the attainment to the equilibrium state, samples prepared in a flow of CO-CO<sub>2</sub> mixture were also melted at 1773K for 2 – 15h in air.

X-ray diffraction studies were carried out with CuK $\alpha$  radiation. The X-ray diffraction profiles showed no traces of crystalline phases, and all samples were found to be amorphous. Mössbauer measurements were carried out at room temperature using 50mCi <sup>57</sup>Co in Rh as the  $\gamma$ -ray source to determine (i) the fraction of  $\text{Fe}^{3+}$  (or  $\text{Fe}^{2+}$ ) ions to the total iron ions and (ii)  $\text{Fe}^{3+}$  ions in tetrahedral (or octahedral) symmetry to the total  $\text{Fe}^{3+}$  ions. The Doppler velocity scale for the measurements was calibrated at room temperature using the spectrum of  $\alpha$ -Fe foil.

## Results

Figure 1 shows a typical Mössbauer spectrum of samples. On the basis of Lorentzian function, this spectrum has been deconvoluted into three symmetrical quadrupole doublets due to  $\text{Fe}^{2+}$  ions in octahedral symmetry and  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral symmetries. The spectra for all the samples have also been deconvoluted in the same manner.

Figure 2 shows the mole percentages (top), the isomer shifts (centre) and the quadrupole splittings (bottom) of  $\text{Fe}^{2+}$  ions in octahedral symmetry and  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral symmetries as a function of melting time. The Mössbauer parameters obtained in this study are close to those reported by Levy et al.(7), who also measured Mössbauer spectra for silicate glasses containing relatively high concentrations of iron oxides (35 mass%  $\text{Fe}_2\text{O}_3$ ). Because Mössbauer parameters are affected by glass compositions, the Mössbauer parameters in this study should be interpreted based upon the study by Levy et al. Thus, it is considered that the doublet with the smallest quadrupole splitting is assigned to  $\text{Fe}^{3+}$  ions in octahedral symmetry. It can be seen from Figure 2 that the ratio of total  $\text{Fe}^{3+}$  ions becomes constant within 2 h after the equilibration operation was started at each temperature. On the other hand, the ratio of  $\text{Fe}^{3+}$  ions in tetrahedral (or octahedral) symmetry becomes constant in about 20 and 6 h for samples melted at 1608 and 1678 K, respectively. This indicates that the structural relaxation requires a longer time than the electronic relaxation. In addition, it is noted that the changes in the isomer shift and quadrupole splitting of  $\text{Fe}^{2+}$  ions correspond to the changes in the percentages of  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral symmetries, which is discussed in Discussion.

Figure 3 shows the percentages (top), the isomer shifts (centre) and the quadrupole splittings (bottom) of  $\text{Fe}^{2+}$  ions in octahedral symmetry and  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral symmetries for the master glass prepared in a flow of CO-CO<sub>2</sub> mixture as a function of melting time, in comparison with the data for samples prepared in air shown in Figure 2. The values of the percentages, the isomer shifts and the quadrupole splittings agree with each other at the end of the equilibration. Thus, it is confirmed that the melts reached the equilibrium during the process.

Figure 4 shows the equilibrium states of iron ions as a function of melting temperature. It is found that the percentages of  $\text{Fe}^{2+}$  ions monotonically increase with increasing the melting temperature, which is in agreement with thermodynamic knowledge that FeO becomes more stable than  $\text{Fe}_2\text{O}_3$  with increasing temperature. It is also found that the fraction of  $\text{Fe}^{3+}$  ions in octahedral symmetry to the total  $\text{Fe}^{3+}$  ions increases with increasing the melting temperature, which is in agreement with the results reported by De Grave et al.(10). The fact that  $\text{Fe}^{3+}$  ions in octahedral symmetry become more stable with increasing temperature indicates that the network structures tend to be more broken at higher temperatures.

## Discussion

According to crystal field theory, the electronic energy of  $\text{Fe}^{3+}$  ions in tetrahedral sites is equal to that of  $\text{Fe}^{3+}$  ions in octahedral sites when  $\text{Fe}^{3+}$  ions are in crystal. However, when  $\text{Fe}^{3+}$  ions are in glass, a small difference would occur between the two energies because of asymmetry in the coordination geometry. This energy difference is relevant to the driving force for the change of  $\text{Fe}^{3+}$  ions in the coordination structure. The small driving force would be the reason that the structural relaxation requires a long time, as mentioned earlier.

The reaction of the change of  $\text{Fe}^{3+}$  ions in the coordination structure is described as follows:

$$\text{Fe}^{3+}(\text{Oh}) = \text{Fe}^{3+}(\text{Td}) \quad (1)$$

The Gibbs free energy change for the reaction is given by

$$G = G^0 + RT \ln(a_{\text{Fe}^{3+}(\text{Td})} / a_{\text{Fe}^{3+}(\text{Oh})}) \quad (2)$$

where  $G^0$  is the standard free energy change,  $R$  is gas constant,  $T$  is the temperature, and  $a_{\text{Fe}^{3+}(\text{Td})}$  and  $a_{\text{Fe}^{3+}(\text{Oh})}$  are the activities of  $\text{Fe}^{3+}$  ions in tetrahedral and octahedral symmetries. Assuming that the activity coefficient of  $\text{Fe}^{3+}$  ions in tetrahedral symmetry is equal to that of  $\text{Fe}^{3+}$  ions in octahedral symmetry, we can write

$$G = G^0 + RT \ln([ \text{Fe}^{3+}(\text{Td}) ] / [ \text{Fe}^{3+}(\text{Oh}) ]) \quad (3)$$

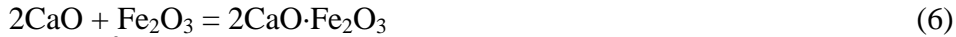
where  $[ \text{Fe}^{3+}(\text{Td}) ]$  and  $[ \text{Fe}^{3+}(\text{Oh}) ]$  are the concentrations of  $\text{Fe}^{3+}$  ions in tetrahedral and octahedral symmetries. At equilibrium,

$$G = 0 = G^0 + RT \ln([ \text{Fe}^{3+}(\text{Td}) ] / [ \text{Fe}^{3+}(\text{Oh}) ]) \quad (4)$$

Then, according to the Gibbs-Helmholtz equation, the standard enthalpy change is expressed as follows:

$$\begin{aligned} H^0 &= \left[ \frac{\partial(DG^0/T)}{\partial(1/T)} \right]_P \\ &= -R \left[ \frac{\partial(\ln([ \text{Fe}^{3+}(\text{Td}) ] / [ \text{Fe}^{3+}(\text{Oh}) ]))}{\partial(1/T)} \right]_P \end{aligned} \quad (5)$$

Figure 5 shows the values of  $[ \text{Fe}^{3+}(\text{Td}) ] / [ \text{Fe}^{3+}(\text{Oh}) ]$  as a function of the reciprocal of temperature, from which the value of  $H^0$  for the reaction of Eq.(1) is calculated as -68.6 kJ/mol. Since  $\text{Fe}^{3+}$  ions occupy the octahedral and tetrahedral sites in  $\text{Fe}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  crystals, respectively, it is reasonable to compare the value of  $H^0$  for the reaction of Eq.(1) with that for the following reaction:



The value of  $H^0$  for the reaction of Eq.(6) is -51.2 kJ/mol at 1400K(18), which indicates that the value of  $H^0$  is -25.6 kJ/mol for 1 mol of  $\text{Fe}^{3+}$  ions. The difference between the experimental value and the estimated one would be due to the reasons that  $\text{Fe}^{3+}$  ions in octahedral symmetry in silicates are more unstable than those in  $\text{Fe}_2\text{O}_3$  and/or that  $\text{Fe}^{3+}$  ions in tetrahedral symmetry in silicates are more stable than those in  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ . However, the estimated value of -25.6 kJ/mol seems to be in agreement with the experimental one as the experimental errors should be large.

With respect to the relaxation mechanism, the possibility is excluded that the structural relaxation proceeds by the diffusion of  $\text{Fe}^{3+}$  ions between tetrahedral and octahedral sites during the equilibration process, for the following reason. If the diffusion of  $\text{Fe}^{3+}$  ions controlled the structural relaxation, the relaxation time would be much shorter than that obtained in the experiment. Thus, it is considered that the rearrangement of oxygen ions dominates the structural relaxation. This consideration is supported by the result that the isomer shifts and quadrupole splittings of  $\text{Fe}^{2+}$  ions change during the equilibration process, as mentioned in Results. The isomer shift is caused by the difference between electron densities at the nuclei of the source and of the absorber. For  $^{57}\text{Fe}$  Mössbauer spectroscopy, the larger isomer shift corresponds to the smaller electron density at the nuclei of the absorber, and the quadrupole splitting is caused by the deviation from the cubic symmetry of ligands. Accordingly, the changes in the Mössbauer parameters of  $\text{Fe}^{2+}$  ions mean the changes in the configuration of ligands around  $\text{Fe}^{2+}$  ions, which is probably due to the rearrangement of oxygen ions in the melts.

## Conclusions

The relaxation of the oxidation state and the coordination structure of iron ions in 40(mol%) $\text{SiO}_2$ -40CaO-20 $\text{Fe}_2\text{O}_3$  melts during the equilibration process has been investigated

using Mössbauer spectroscopy.

- The fraction of  $\text{Fe}^{3+}$  ions to the total iron ions became constant within 2 h after the equilibration operation was started. On the other hand, it took about 20 and 6 h for the coordination structures of  $\text{Fe}^{3+}$  ions to settle down by sharing between tetrahedral and octahedral sites when the samples were melted at 1608 and 1678K, respectively. In addition, the changes in the isomer shift and quadrupole splitting of  $\text{Fe}^{2+}$  ions corresponded to the changes in the percentages of  $\text{Fe}^{3+}$  ions in octahedral and tetrahedral symmetries. From these results, it has been considered that the relaxation of structural coordination of the melts proceeds by rearrangement of oxygen ions rather than by the diffusion of iron ions in the silicate melts.
- The fraction of  $\text{Fe}^{3+}$  ions in tetrahedral symmetry to the total  $\text{Fe}^{3+}$  ions at equilibrium decreases with increasing temperature. The standard enthalpy change for the reaction of the change of  $\text{Fe}^{3+}$  ions in the coordination structure was calculated as -68.6kJ/mol. This indicates that the network structures tend to be more broken at higher temperatures.

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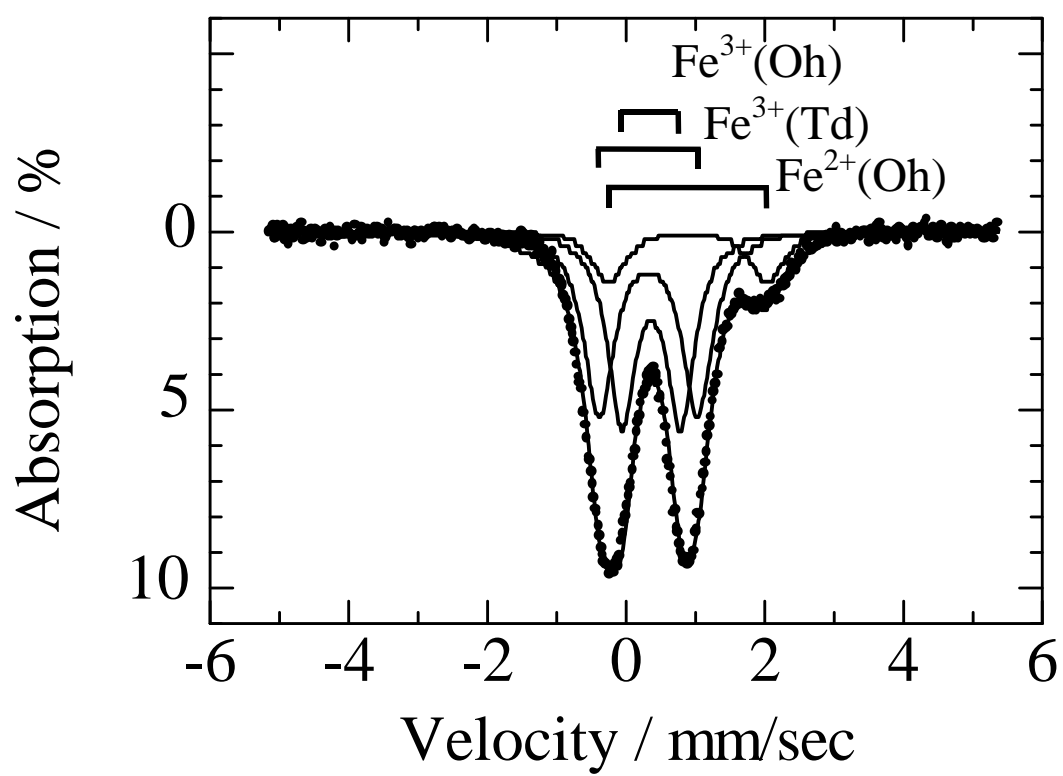


Fig.1 A typical Mössbauer spectrum of samples.

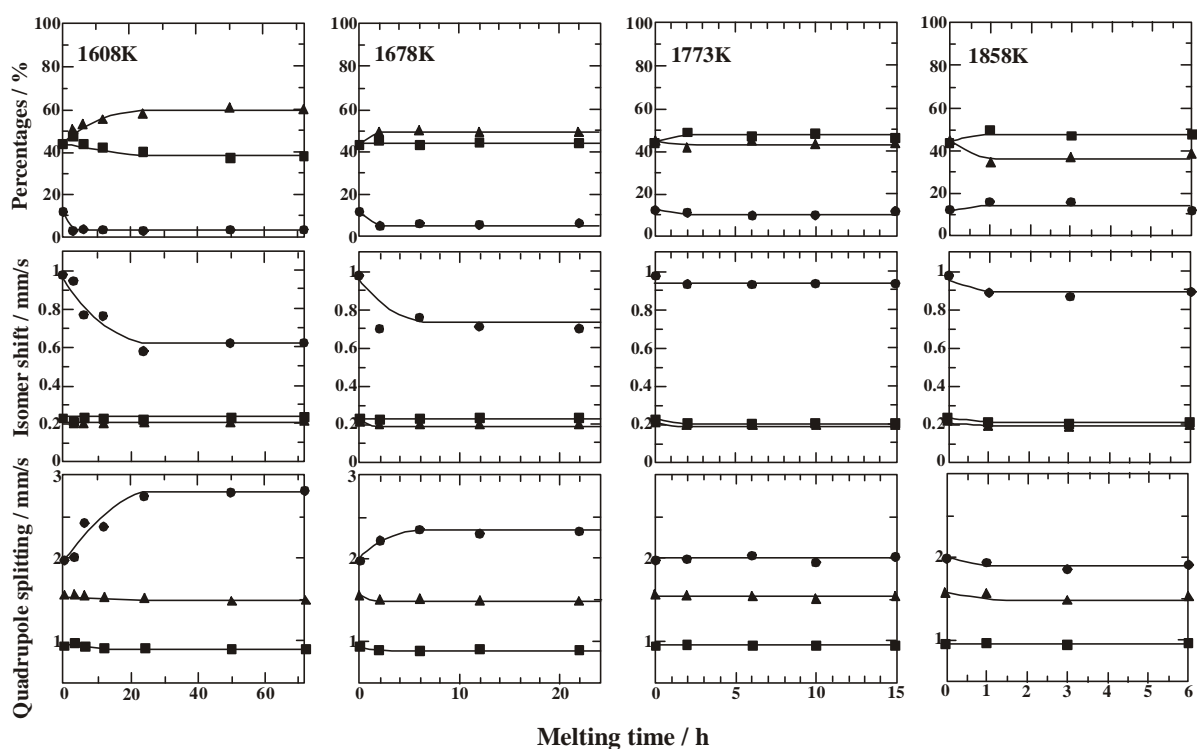


Fig.2 Percentages (top), isomer shifts (centre) and quadrupole splittings (bottom) of Fe<sup>2+</sup> ions in octahedral symmetry ( ) and Fe<sup>3+</sup> ions in octahedral ( ) and tetrahedral ( ) symmetries as a function of melting time.

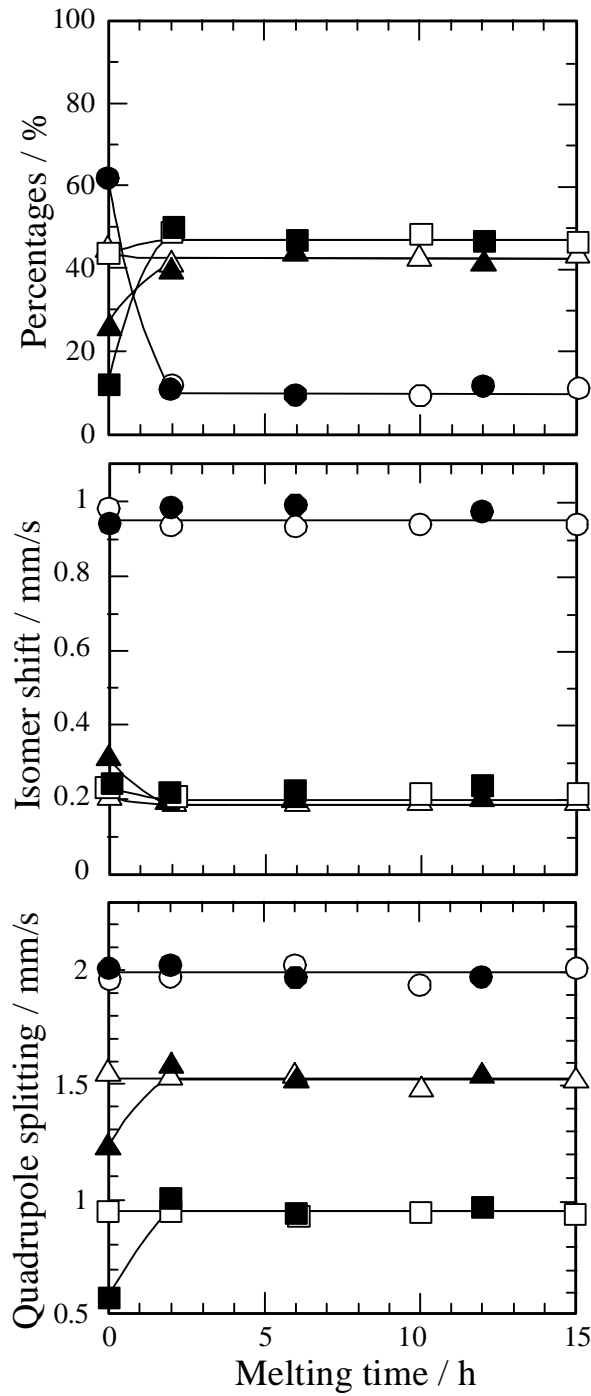


Fig.3 Percentages (top), isomer shifts (centre) and quadrupole splittings (bottom) of Fe<sup>2+</sup> ions in octahedral symmetry (○) and Fe<sup>3+</sup> ions in octahedral (□) and tetrahedral (△) symmetries for the master glass prepared in a flow of CO-CO<sub>2</sub> mixtures as a function of melting time, in comparison with the data of Fe<sup>2+</sup> ions in octahedral symmetry (●) and Fe<sup>3+</sup> ions in octahedral (■) and tetrahedral (▲) symmetries for the samples prepared in air.



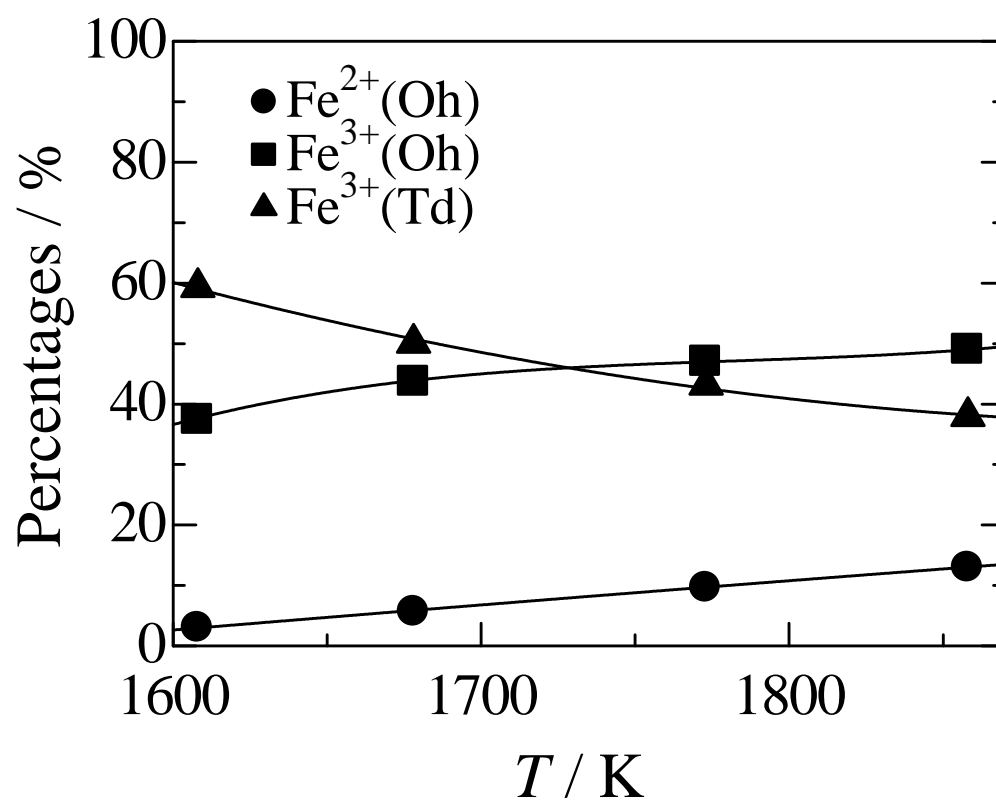


Fig.4 Equilibrium states of iron ions as a function of the melting temperature.

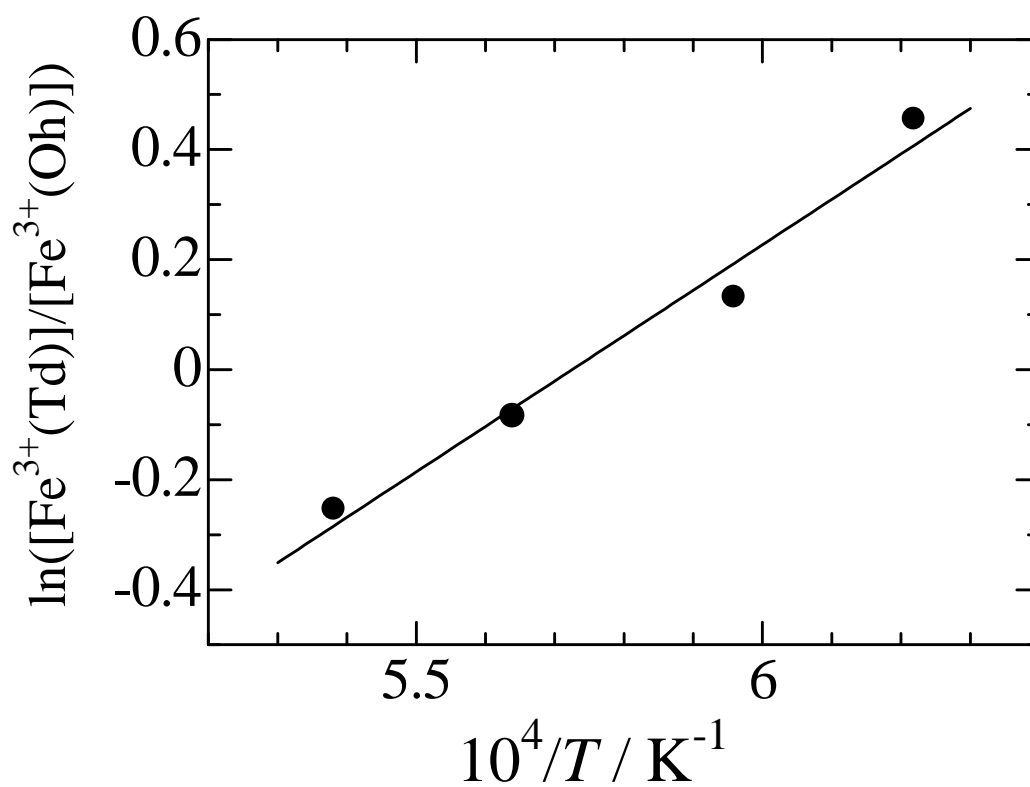


Fig.5 The values of  $\ln([Fe^{3+}(Td)]/[Fe^{3+}(Oh)])$  as a function of the reciprocal of temperature.