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Dissociation Pressure of Ferric Oxide

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The dissociation pressure of various oxides was measured in a high vacuum, and the results were found to be in good agreement with the values calculated from standard free energy data.[1)] However, it was also found that all metallic oxides evolved a large amount of carbon monoxide and carbon dioxide at lower temperatures.

Direct measurement of the oxygen dissociation pressure of ferric oxide at high temperatures is desirable. It is of interest to study the evolution of gases during the course of the reduction of ferric oxide by vacuum heat teratment.[2)]

In the present experiment, the equilibrium pressures of ferric oxide and the desorbed gases have been measured with a McLeod gauge and the percentage compositions of the gases have been investigated by means of an omegatron mass spectrometer.

Experimental

The apparatus was similar to that described previously.[1)] The sample of ferric oxide (α-type, diamagnetic) was a Merk reagent of extra pure grade (Germany) and was used without further purification.

Measurements were carried out under various initial conditions of the samples. In the first run, a freshly powdered sample of about 500 mg was placed in the decomposition cell and evacuated for a day in a high vacuum at room temperature. The sample was then heated to 300°C. The equilibrium pressure of the evolved gases was measured by a McLeod gauge and analyzed by an omegatron mass spectrometer. A similar procedure was repeated at temperatures from 300 to 1200°C. The sample which was heated to 1200°C in the first run was cooled in a vacuum and used again in the second run. The same procedure was repeated in the second run. Replacing the sample with a new one, the measurement was repeated several times.

Results and Discussion

Carbon dioxide, methane, and water were evolved from the new samples below 600°C and in some cases total pressure of these gases amounted to 10^{-3} Torr. However, the evolution of these gases decreased after the first vacuum heat treatment, and the reproducibility of the equilibrium pressures could not be obtained in different runs. On the other hand, the amount of carbon monoxide increased with the oxygen evolution at higher temperature and reproducible equilibrium pressure was attained ($P_{CO}=2\times 10^{-2}$ Torr at 1150°C).

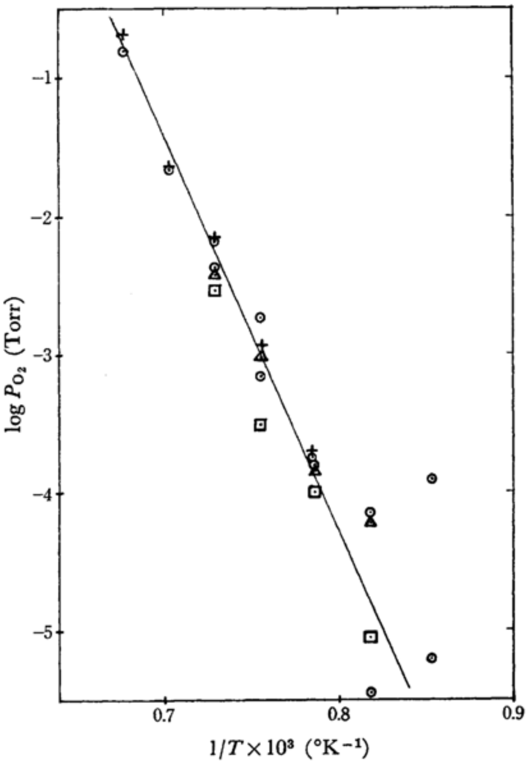

Fig. 1. Dissociation pressure of ferric oxide *vs.* $1/T$.
The values of different symbols show different runs.

Oxygen gas resulting from thermal decomposition can be observed above 900°C. In Fig. 1 the equilibrium pressures of oxygen are plotted against the reciprocal of the absolute temperatures. The straight line obtained in Fig. 1 can be represented by the following equation.

$$\log P_{O_2}\ (\text{Torr}) = -\frac{28.5}{T}\times 10^3 + 18.5 \qquad (1)$$

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1) K. Kodera, I. Kusunoki and S. Shimizu, This Bulletin, **41**, 1039 (1968); *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 814 (1965).

2) M. Onchi and I. Kusunoki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 612, 619 (1964).

The sample treated in the second run was analyzed by means of X-ray diffraction and confirmed to be a mixture of oxides Fe_2O_3 and Fe_3O_4. On the other hand, it was confirmed by X-ray analysis that the sample evacuated in vacuum at 1200°C for a day transformed into magnetite (Fe_3O_4, ferromagnetic). The sample did not evolve oxygen gas further at 1200°C. This result is consistent with the report[3] in which the preparation of Fe_3O_4 by heating Fe_2O_3 up to 1300°C in a vacuum was described.

Thus the reaction in the present experiment may be written as

$$6Fe_2O_3(s) \rightleftarrows 4Fe_3O_4(s) + O_2, \qquad (2)$$

and the standard free energy change, $\varDelta G°$, for the reaction may be given by

$$\varDelta G°(\mathrm{cal}) = 130600 - 71.51T. \qquad (3)$$

On the other hand, the value obtained by Richardson and Jefes[4] is shown as

$$\varDelta G°(\mathrm{cal}) = 119240 - 67.24T. \qquad (4)$$

These values are in good agreement in the temperature range of measurement.

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[3] L. Brewer and D. Mastick, *J. Chem. Phys.*, **19**, 834 (1951).

[4] F. D. Richardson and J. H. E. Jefes, *J. Iron Steel Inst.*, **160**, 261 (1948); **163**, 397 (1947).