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The Thermodynamic Properties of the Wustite Phase Are Studied

The thermodynamic properties of the wustite (FeO_{1+x}) phase have been measured over a temperature range of 970–1280°K by determining the values of x for known oxygen pressures. The study was conducted by R. J. Ackermann and R. W. Sandford, Jr. of Argonne National Laboratory, Argonne, Illinois, and their complete findings have been published in "A Thermodynamic Study of the Wustite Phase," ANL-7250, September 1966. In the report, free energies, enthalpies and entropies, as well as their respective trends with composition and temperature, were derived from the measured quantities, the Gibbs-Duhem equation and colorimetric data. The behavior of the partial molar quantities of oxygen and iron suggest the existence of a complicated temperature-dependent microstructure or superstructure.

The immediate goals of the present study were to determine: 1) the precise location of the wustite phase boundaries, and 2) the dependence of the partial pressure of oxygen on the temperature and composition of the solid phase. The concentration of effort was in the range of 950° to 1300°K where the behavior is of major interest.

The characteristics of the vaporization behavior of refractory metal-oxide systems have been a problem extensively studied in high-temperature chemistry. This involves not only the identification of the various vapor species over a condensed phase, but also the determination of the chance in frec energy, enthalpy, and entropy that accompany vaporization. The problem which has complicated the thermodynamic analysis of almost every vaporization study is the uncertainty of the thermodynamic properties of the solid phase which result from its deviation from known stoichiometry at the high temperatures necessary to produce measurable vaporization.

Many investigators have studied the iron–oxygen system, particularly the FeO_{1+x} region. Nevertheless a clear understanding of the system required further study, especially at temperatures less than 1000°C, because of numerous discrepancies in previous studies and because of the current use of an iron-wustite electrode as a standard for the high-temperature, solid-galvanic-cell determinations of the partial molar free energy of oxygen in nonstoichiometric metal oxides.

To determine the partial pressure of oxygen over a known composition of wustite at a given temperature, a system was devised for controlling and determining the three experimental variables of the macroscopic system (the pressure of oxygen, the temperature, and the composition of the solid phase). By applying the phase rule, the wustite phase was known to have two degrees of freedom. Thus when any two of the three variables are controlled, the third is fixed. The experiment was designed to control the pressure of oxygen and the temperature, and to determine the composition of FeO_{1+x} as a function of these controlled variables.

From the pressure of oxygen, the temperature and the composition, the thermodynamic quantities including the free energy, enthalpy, and entropy can be determined.

(continued overleaf)

Notes:

1. A better understanding of the FeO system may be of interest to metallurgists and those using refractories.
2. The report is available from Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 22151: price $3.00 (microfiche $0.65). Inquiries may also be directed to:

   Office of Industrial Cooperation
   Argonne National Laboratory
   9700 South Cass Avenue
   Argonne, Illinois 60439
   Reference: B68-10408

Source: R. J. Ackerman, R. W. Sandford, Jr.
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Patent status:

Inquiries about obtaining rights for commercial use of this innovation may be made to:

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