# MICROTHERMOGRAVIMETRIC STUDIES OF THE KINETICS AND THERMODYNAMICS OF HETEROGENEOUS REACTIONS IN SULFUR-CONTAINING ATMOSPHERES

*M. Danielewski* and *S. Mrowec*

INSTITUTE OF MATERIALS SCIENCE, ACADEMY OF MINING AND
METALLURGY, CRACOW, POLAND

A thermobalance for studies of the high-temperature sulfidation of metals and alloys is described. This apparatus permits the determination of mass changes in the sulfidized sample as functions of temperature and sulfur vapour pressure with an accuracy of $10^{-6}$ g. Besides heterogeneous kinetics measurements, it has been shown that the chemical diffusion coefficients and deviations from stoichiometry of metal sulfides can also be studied as functions of temperature and sulfur pressure by means of equilibration measurements.

The interest in thermogravimetry for study of the physico-chemical properties of solids and the kinetics and mechanisms of heterogeneous reactions has increased greatly during the past twenty years [1, 2]. However, this important experimental methods has mainly been applied to reactions with oxygen, as other oxidants, such as sulfur and halogens, make the measurements much more difficult. Like bromine and iodine, sulfur, exists in the condensed state under normal conditions, and this together with the very aggressive nature of the vapor precludes thermogravimetric measurements in standard equipment. On the other hand, there is an urgent need for the better understanding of the physico-chemical properties of metal sulfides and the high-temperature sulfide corrosion of metallic materials. Thus, many attempts are being made to adapt thermogravimetry for studies on the kinetics of metal sulfidation and on defect structures and diffusion in metal sulfides.

The kinetics of high-temperature sulfidation of metals, as well as mass changes of sulfides, can be measured either in sulfur vapor or in $H_2/H_2S$ gas mixtures. The latter allows measurements at relatively low partial pressures of sulfur, not exceeding $10^{-3}$ atm. Measurements at higher sulfur vapor pressures require the application of liquid sulfur to produce sulfur vapor of appropriate pressure. In contrast to $H_2/H_2S$ gas mixtures, where the measurements are relatively simple, in an atmosphere of sulfur vapor the situation is much more complicated, due to the possibility of condensation of sulfur on the cool parts of the equipment. However, in both cases the same dif-

ficulties are encountered in measuring the sulfur vapor pressure in the reaction cham-
ber. Further, the mass changes can only be measured using a spiral balance made of
highly corrosion-resistant materials. In practice the quartz spiral balances also used
in oxygen atmospheres are suitable.

In the present paper a new microthermobalance for the study of high-temperature
reactions in sulfur is described. This apparatus permits not only mass change recording
with high precision, but also direct measurement of sulfur vapor pressure [3].

The scheme of the microthermobalance is shown in Fig. 1. The main parts of this
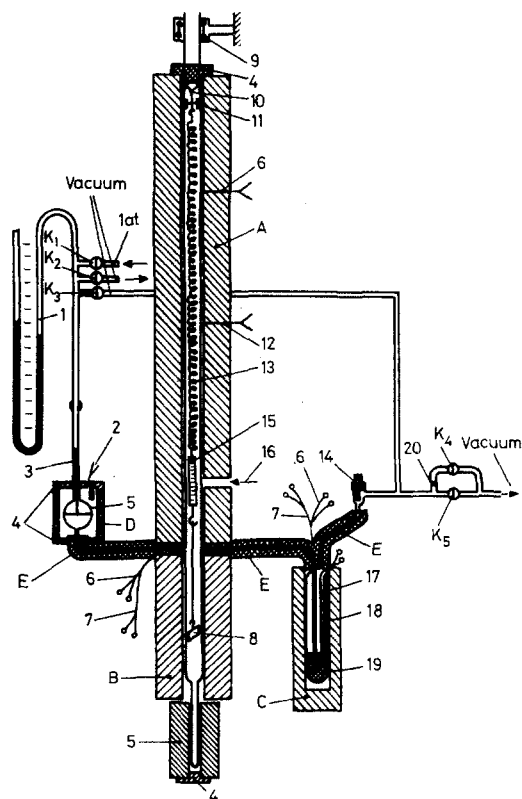apparatus are as follows: the container with liquid sulfur, the reaction chamber with



**Fig. 1** Scheme of thermogravimetric apparatus for studying defect equilibria in sulfides and
kinetics of metal sulfidation. 1 — mercury manometer, 2 — thermoelement, 3 — quartz rod
showing deflections of membrane, 4 — thermal insulation, 5 — quartz membrane manom-
eter, 6 — regulating thermoelements, 7 and 12 — thermoelements controlling temperature of
furnaces, 8 — sample, 9 — clamps fixing reaction tube, 10 and 11 — suspension of spiral,
13 — quartz spiral, 14 — vacuum valve, 15 — scale for reading elongation of spiral, 17 — ad-
ditional heating element for sulfur, 18 — screen of heating element, 19 — sulfur, 20 — Pyrex
glass—quartz joints, $K_1$–$K_5$ — vacuum taps, A — furnace thermostating spiral, B — reaction
furnace, C — sulfur-heating furnace, D — furnace thermostating sulfur vapor leads

the quartz spiral space, and the quartz membrane manometer. All parts of the apparatus are made of quartz and are equipped with thermostating furnaces. The upper part containing the spiral is thermostated with an accuracy of ±0.3 degree, the temperature of this space, and of all leads of sulfur vapor from the sulfur container to the reaction chamber. The temperature of the liquid sulfur is controlled with an accuracy of ±0.1 degree, sulfur vapor pressure being very sensitive to temperature fluctuations. The sulfur vapor pressure in the reaction chamber is measured with a membrane manometer (Fig. 2) by compensating the pressure of sulfur vapor on the membrane
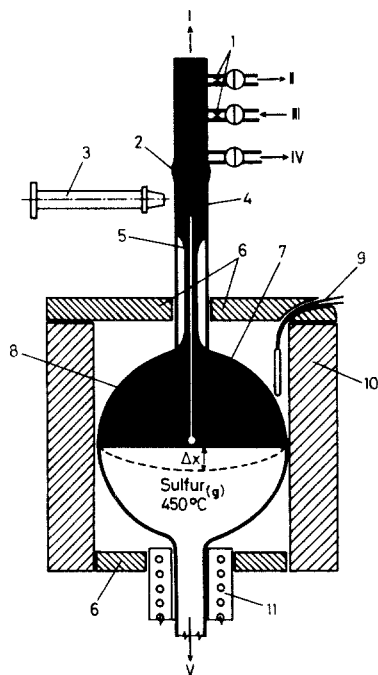


**Fig. 2** Scheme of membrane manometer for measuring sulfur vapor pressure in reaction chamber of microthermobalance. I — to mercury manometer, II — to vacuum pump, III — air, IV — connection to vacuum system of microthermobalance, V — connection to reaction chamber; 1 — capillaries, 2 — Pyrex glass—quartz joint, 3 — microscope, 4 — quartz rod, 5 — tube leading to quartz rod, 6 — thermal insulation, 7 — quartz vessel, 8 — quartz membrane, 9 — thermoelement, 10 — furnace thermostating membrane, 11 — furnace thermostating connections to reaction chamber

by the pressure of air from the other side of the membrane, and determination of this pressure with a mercury manometer. The quartz thread spiral (dia. 0.2 mm), consisting of 50 coils (dia. 30 mm), permits recording of mass changes in the sample (about 1 g) with an accuracy of $10^{-6}$ g. This sensitivity corresponds to that of modern microthermogravimetric devices for oxygen atmospheres. The quartz spiral is suspended in the reaction tube on a special arrangement allowing its vertical movement with an electromagnet. This makes it possible to suspend and remove the

specimen from the apparatus after the reaction tube has been opened from the bottom. After the specimen has been suspended and the reaction tube closed, the system is evacuated and the reaction chamber is heated to the appropriate temperature. When the temperature reaches a constant value, the sulfur container is heated to the temperature corresponding to the sulfur vapor pressure needed. Depending on its value, the constant pressure in the reaction chamber is attained after 3—5 minutes. The mass changes in the sample during the reaction are recorded with a cathetometer with an accuracy of ±0.001 cm.

In order to illustrate the applicability of the apparatus described above, the results on the kinetics of iron sulfidation, deviations from stoichiometry, and self-diffusion and chemical diffusion in iron(II) sulfide are presented.

The iron—iron(II) sulfide—sulfur system has been extensively studied [4—9], but due to the above-mentioned experimental difficulties the results obtained so far are controversial. Our experiments have been carried out at temperatures ranging from 650 to 900° and sulfur vapor pressures from $10^{-3}$ to 0.8 atm. In Fig. 3, results are presented on iron sulfidation kinetics at 700° for various sulfur vapor pressures. It can be seen that the growth of sulfide scale on iron follows a parabolic rate law, which means that the rate-determining step of the overall reaction is the outward diffusion of iron. Iron(II) sulfide is, a metal-deficient compound ($Fe_{1-y}S$), predominant defects being cation vacancies [10]. Figures 4 and 5 depict the pressure and temperature-dependences of the parabolic rate constant of iron sulfidation. It follows from these plots that the above apparatus permits determination of the influence of both these parameters on sulfidation kinetics.

After complete sulfidation of iron specimens, the mass changes of iron(II) sulfide were studied as functions of temperature and sulfur vapor pressure, in order to determine the deviations from stoichiometry and consequently the cation vacancy concentrations. These results are presented in Fig. 6. The reequilibration kinetics of iron(II) sulfide have also been studied as functions of both parameters, to evaluate the chemical diffusion coefficients in this material. It has been shown that this co-
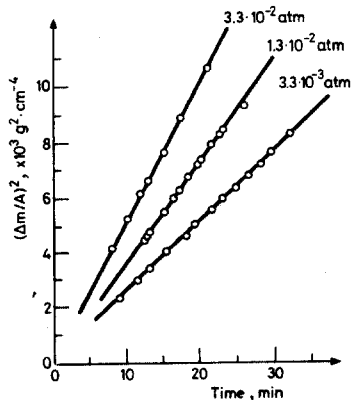
Fig. 3 Kinetics of iron sulfidation at 970 K, presented in parabolic plot for several vapor pressures
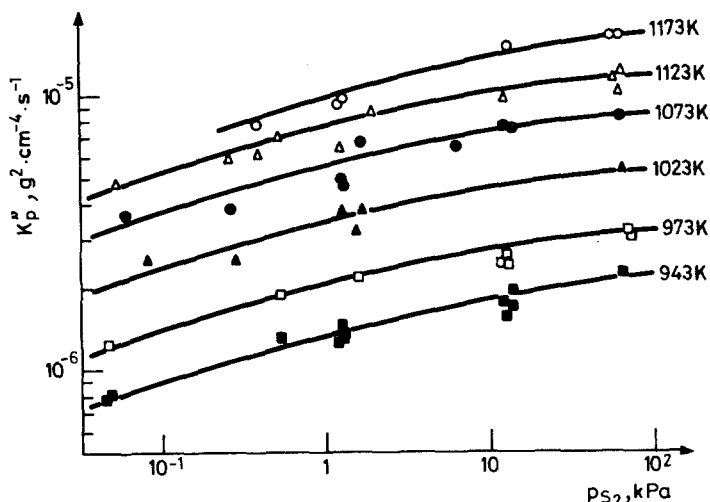
**Fig. 4** Dependence of parabolic rate constant of iron sulfidation on sulfur vapor pressure for several temperatures
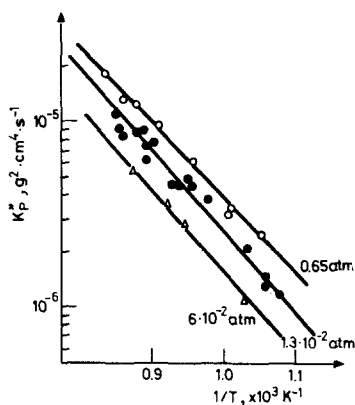


**Fig. 5** Dependence of parabolic rate constant of iron sulfidation on temperature of several sulfur vapor pressures

efficient depends only on the temperature, but not on the sulfur vapor pressure (Fig. 7).

The results described above allowed the self-diffusion coefficient of iron in iron(II) sulfide to be calculated as functions of temperature and sulfur vapor pressure. Consequently, the activation energy of iron diffusion and the mobility of cation vacancies in $Fe_{1-y}S$ could be determined. Figures 8 and 9 illustrate the dependences of the self-diffusion coefficient of iron and the defect-diffusion coefficient in iron(II) sulfide on the non-stoichiometry. These results made it possible to check the Libowitz [14]
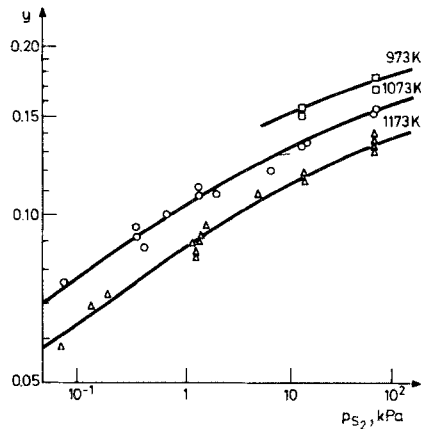
Fig. 6 Dependence on non-stoichiometry of iron(II) sulfide, $Fe_{1-y}S$, on sulfur vapor pressure for several temperatures
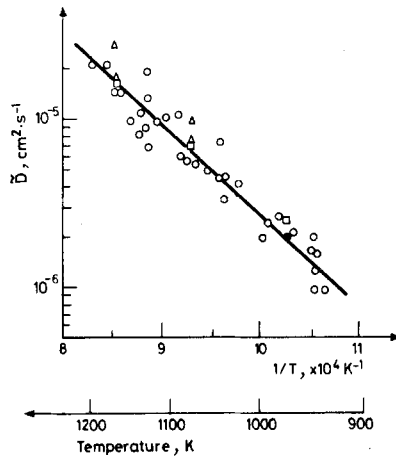


Fig. 7 Dependences of chemical diffusion coefficient in iron(II) sulfide on temperature. □ Smeltzer et al. [11], △ Turkdogan [12], ○ this work

theory, which assumes strong repulsive interactions between cation vacancies, due to which the concentration of defects decreases with increasing temperature (Fig. 4).

The above-described example illustrates well the applicability of microthermo-gravimetry for study of the kinetics and mechanisms of the high-temperature sulfide corrosion of metallic materials, as well as defect structure and diffusion processes in metal sulfides. These measurements are in fact more complicated than those in oxygen, but they provide equally precise data concerning not only the kinetics of high-

temperature heterogeneous reactions, but also deviations from stoichiometry and the transport properties of sulfides. The apparatus described in this paper is now being used succesfully to study other sulfide systems [15].
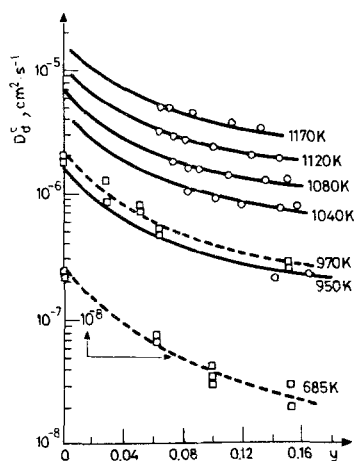


**Fig. 8** Dependence of defect diffusion coefficient in $Fe_{1-y}S$ on non-stoichiometry



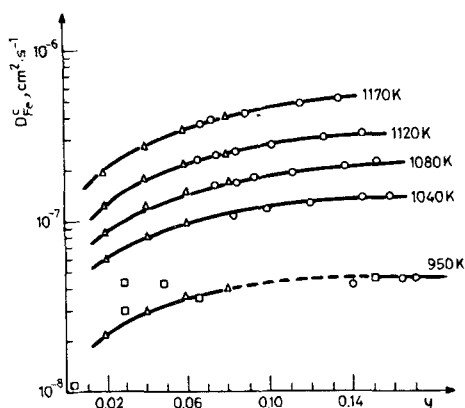**Fig. 9** Dependence of self-diffusion coefficient of iron in iron(II) sulfide on non-stoichiometry for several temperatures. □ Birchenall et al. [13], △ Smeltzer et al. [11], ○ this work

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**Zusammenfassung** — Es wird eine Thermowaage zur Untersuchung der Hochtemperatur-Sulfidierung von Metallen und Legierungen beschrieben. Diese Apparatur ermöglicht die Bestimmung von Massenveränderungen der sulfidierten Proben in Abhängigkeit von der Temperatur und dem Schwefeldampfdruck mit einer Genauigkeit von $10^{-6}$ g. Es wird gezeigt, daß damit, sofern Gleichgewichtsmessungen ausgeführt werden, auch die chemischen Diffusionskoeffizienten und Abweichungen der Metallsulfide von der Stöchiometrie in Abhängigkeit von der Temperatur und dem Schwefeldampfdruck untersucht werden können.

**Резюме** — Описаны термовесы для изучения высокотемпературного сульфидирования металлов и сплавов. Аппаратура позволяет определять изменение веса сульфидируемого образца в зависимости от температуры и давления паров серы с точностью $10^{-6}$ г. Показано, что, за исключением гетерогенных кинетических измерений, коэффициенты химической диффузии и отклонения от стехиометрии сульфидов металлов могут быть также изучены в зависимости от температуры и давления серы с помощью равновесных измерений.