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Fig. 1. Schematic drawing of the apparatus: 1 –Knudsen vessel (made of tantalum); 2 –lower ground joint; 3 –flange of the pumping system; 4 –ground joint of the condensation device; 5 –cooler; 6 –holder of the Knudsen vessel; 7 –regulating thermocouple; 8 –measuring thermocouple; 9 –targets; 10 –shutter; 11 –receiver of the exposed targets; 12 –collimator

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Abstract

Full Text

PHYSICAL CHEMISTRY

E. Z. VINTAIKIN

DETERMINATION OF THE VAPOR PRESSURE OF IRON OVER AUSTENITE

(Presented by Academician G. V. Kurdiumov, May 22, 1956)

The iron-carbon system, which is of great practical importance, has repeatedly been subjected to thermodynamic investigations. In a number of studies, culminating in the work of Smith$^{(1)}$, carried out at a high experimental level, the equilibrium of carbon dissolved in metal with gas mixtures $CO-CO_2$ and CH_4-H_2 was investigated. In these works it was established that the heat of solution of carbon in γ-iron does not depend on the carbon concentration and is approximately equal to 10 kcal/g-atom. It was also established that in solutions of carbon in γ-iron a noticeable deviation from the laws of ideal dilute solid solutions is manifested: the activity of carbon increases with increasing concentration more rapidly than a linear function.

In work $^{(2)}$ the causes of the nonideality of the solution of carbon in γ-iron are discussed. The authors, proceeding from the assumption that the partial heat contents of the components do not depend on concentration, and also taking into account the specific character of an interstitial solid solution, derive an equation for the activity coefficient of carbon in austenite that agrees with Smith' s experimental data $^{(1)}$.

Fig. 1. Schematic drawing of the apparatus:
1 –Knudsen vessel (made of tantalum); 2 –lower ground joint; 3 –flange of the pumping system; 4 –ground joint of the condensation device; 5 –cooler; 6 –holder of the Knudsen vessel; 7 –regulating thermocouple; 8 –measuring

Fig. 2. Temperature dependence of the vapor pressure of pure iron

Figure 2: Fig. 2. Temperature dependence of the vapor pressure of pure iron

thermocouple; 9 –targets; 10 –shutter; 11 –receiver of the exposed targets; 12 –collimator

Work (3) is devoted to the investigation of the thermodynamic properties of austenite; it was carried out by measuring vapor pressure by the Knudsen method. In this work, from data on the temperature dependence of the vapor pressure of iron, the heats of sublimation were determined for pure iron and also for alloys with carbon. The heat of sublimation for pure γ-iron amounted to 103.5 kcal/g-atom, and for austenite with 4.5 and 5.8 at.% C, respectively, to 54.6 and 43.5 kcal/g-atom. Thus, from the results of this work it follows that the heat of dilution of iron $\Delta\bar{H}_{\mathrm{Fe}}$ depends very strongly on the carbon concentration: at a carbon content of 4.5 at.% it

is equal to +48.9 kcal/g-atom, and at 5.8 at.% C $\Delta\overline{H}_{\mathrm{Fe}} = +60$ kcal/g-atom. Meanwhile, in the work of Smith (1) it is asserted that the heat of solution of carbon in austenite does not depend on the concentration.

Thus, the data of Smith (1) and Kornev (3) contradict one another, failing to satisfy the Gibbs–Duhem equation.

$$x_{\mathrm{Fe}}\frac{\partial\Delta\overline{H}_{\mathrm{Fe}}}{\partial x_{\mathrm{Fe}}} = x_{\mathrm{C}}\frac{\partial\Delta\overline{H}_{\mathrm{C}}}{\partial x_{\mathrm{C}}}. \tag{1}$$

It should be noted that Smith’ s data were partially confirmed by work (4), in which the authors studied the equilibrium of carbon dissolved in austenite with a CO–CO_2 gas mixture.

The present work is devoted to determining the thermodynamic characteristics of austenite in order to check and refine Kornev’ s results (3).

In this work the vapor pressure of iron over austenite was determined by the Knudsen method with the aid of the radioactive isotope Fe^{59}. A diagram of the apparatus is given in Fig. 1*.

Pure iron and alloys with 2.7 and 4.3 at.% C were investigated in the temperature range 1150–1350°. Electrolytic iron, which had been activated in a physical reactor, was used to prepare the samples. The alloys with carbon were prepared by melting pure iron with synthetic cast iron in a helium atmosphere. Since no burning-off of carbon occurred, the composition of the alloys was determined from the charge data.

Fig. 2. Temperature dependence of the vapor pressure of pure iron

The results of the experiments are presented in Figs. 2 and 3, in which each experimental point corresponds to the average of 2 or 3 measurements. It should

Fig. 3. Temperature dependence of the vapor pressure of iron over austenite; A –2.7 at.% C; B –4.3 at.% C

Figure 3: Fig. 3. Temperature dependence of the vapor pressure of iron over austenite; A –2.7 at.% C; B –4.3 at.% C

be noted that all experiments were carried out in such a way that the low-temperature points corresponded to the first measurements. From Fig. 3 it is seen that at low temperature the points do not fall on the straight line, but somewhat above it. Moreover, the vapor-pressure values at low temperatures are not reproduced, since the measured quantities tend to decrease. In Fig. 3A the low-temperature points represent the average of 3 measurements (each measurement lasted 1 hour), which may differ from one another by as much as 80%. Taking all these circumstances into account, it is natural to suppose that at low temperatures the sample was in a nonequilibrium state.

It is known that in iron and in its alloys, owing to the $\alpha \to \gamma$ transformation, recrystallization occurs, as a result of which the metal grains undergo phase work-hardening. In such grains the free energy is somewhat increased. Evidence for this is the recrystallization of austenite upon raising the temperature, in which grains with a distorted crystal lattice are replaced by very fine grains with a regular lattice. All this should lead to a certain increase in vapor pressure at temperatures slightly above the recrystallization temperature.

To check this supposition, the following experiment was carried out. After measurements at low temperatures (Fig. 3A, point 1), the sample was held at 1300° (point 2), then measurements were again made at low temperatures (point 3); the last point fell on the straight line. After this, without breaking the vacuum, the sample was cooled to room temperature,

* A more detailed description of the method used in this work may be found in work (^{6}).

and then measurements were again carried out (point 4); from Fig. 3A it is seen that point 4 falls out of the straight-line dependence. Thus, those low-temperature points on the graphs which lie above the straight line correspond to a thermodynamically nonequilibrium state of austenite and should not be included in the calculation. It is interesting to note that for pure iron such an effect was not detected. This may be explained by the fact that in pure iron the effect is so small that, with the existing accuracy of the experiment, it could not be detected.

Fig. 3. Temperature dependence of the vapor pressure of iron over austenite; A –2.7 at.% C; B –4.3 at.% C

Processing of the experimental data for pure iron leads to the following temperature dependence of the vapor pressure (expressed in dyn/cm^2):

$$\lg p = -\frac{20630}{T} + 12.70. \tag{2}$$

It should be noted that the results for pure iron differ somewhat from the data reported in work ([3]), but they agree with the results of work ([5]).

The heats of sublimation calculated from the data of the present work proved to be as follows: for pure iron, 94.5 kcal/g-atom; for alloys with 27 at.% C, 95.0 kcal/g-atom; and for 4.3 at.% C, 89.3 kcal/g-atom.

Thus, the heat of sublimation is almost independent of the carbon content. This is in good agreement with the data of Smith ([1]). The strong dependence of the heat of sublimation on carbon content obtained by Kornev is apparently a consequence of the fact that in his work the measurements were carried out at lower temperatures than in the present work. In this case, as follows from our data, the measured vapor pressures referred to the nonequilibrium state of austenite, changing in the course of the experiment.

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