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Abstract

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ON THE RELATION BETWEEN THE THERMODYNAMIC PROPERTIES OF AUSTENITE AND ITS STRUCTURE

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Information on the thermodynamic activity of carbon dissolved in iron can be very useful in considering a number of theoretical and applied problems of metallurgy and metal science. From these data one can obtain values of the free energy of formation of alloys in the iron–carbon system, which are necessary when considering phase transformations in this system.

Experimental determination of the thermodynamic activity of carbon dissolved in austenite, as a function of temperature and carbon concentration, has repeatedly been carried out in studies of the equilibrium of carburizing reactions of iron with gas mixtures containing carbon. In [1] it was shown that the most reliable data can be obtained in studying the reaction

$$C + 2H_2 = CH_4, \qquad K = P_{CH4}/P_{H2}^2 a_C, \tag{1}$$

where C refers to carbon dissolved in iron, K is the equilibrium constant, P_{CH4} and P_{H2} are the partial pressures of methane and hydrogen in equilibrium with an alloy of the given concentration; a_C is the activity of carbon. To determine the activity of carbon relative to graphite, the values of K for the equilibrium of reactions (1) with graphite were used.

The equilibrium of reaction (1) was investigated in works [1–3] over a wide range of concentrations and temperatures. The results of these investigations agree excellently with one another. In a number of studies, attempts were made to establish a relation between the thermodynamic characteristics and the structure of phases in the iron–carbon system. A review of such works is contained in [4,5]. However, the consideration carried out in these works was based on insufficiently reliable and incomplete experimental data and on incorrect ideas about the structure of austenite, and the approximate agreement of the equations obtained with experiment could not serve as a basis for any definite conclusions.

At present it is generally accepted that austenite is an interstitial solution and that carbon atoms are located at the centers of octahedral voids between iron

atoms. An attempt to describe the dependence of the activity of carbon on concentration, treating austenite as an interstitial solution, was undertaken as early as ([6]). It was assumed that carbon atoms occupying neighboring octahedral voids do not interact with one another. In this case the activity of carbon should be proportional to the ratio of the number of occupied sites to the number of vacant sites. Since the number of octahedral voids in the austenite lattice is equal to the number of iron atoms,

$$a_{\mathrm{C}} \sim n_{\mathrm{C}}/(n_{\mathrm{Fe}} - n_{\mathrm{C}}), \tag{2}$$

where n_{C} and n_{Fe} are the numbers of carbon and iron atoms. However, it turned out that the experimentally determined values of a_{C} increase more strongly with increasing carbon concentration than is prescribed by equation (2).

A similar consideration was carried out in ([7]); however, in ([7]) it was assumed that carbon atoms occupying neighboring octahedral voids repel one another. In accordance with this assumption, in ([8]) an equation was obtained for the activity of carbon in austenite relative to the infinitely dilute solution,

$$\ln a_{\mathrm{C}} = \ln (N_{\mathrm{C}}/N_{\mathrm{Fe}}) + 6.6 N_{\mathrm{C}}/N_{\mathrm{Fe}}, \tag{3}$$

where N_{C} and N_{Fe} denote the atomic fractions of carbon and iron in austenite. However, equation (3) was obtained from data for the reaction $\mathrm{C} + \mathrm{CO}_2 = 2\mathrm{CO}$, where the concentration dependence of the activity of carbon is affected by oxygen dissolving in austenite. Equation (3) differs appreciably from the experimental data for reaction (1).

A different interpretation of the results on determining the activity of carbon in austenite is given in ([9]). In that work it was assumed that deviations from ideality in austenite are explained not so much by the interaction energy between carbon atoms as by the limited number of sites into which carbon can enter. In ([9]) it was assumed that only 1/4 of the octahedral voids in the iron lattice can be used for the incorporation of carbon atoms. In this case the number of possible energetically equivalent states is given by the relation

$$W = (\tfrac{1}{4} n_{\mathrm{Fe}})!/n_{\mathrm{C}}!(\tfrac{1}{4} n_{\mathrm{Fe}} - n_{\mathrm{C}})!. \tag{4}$$

The expression obtained from this after transformation for the activity of carbon in austenite relative to the infinitely dilute solution has the form

$$a_{\mathrm{C}}^{\infty} = N_{\mathrm{C}}/(1 - 5N_{\mathrm{C}}). \tag{5}$$

Equation (5) gives the best description of the experimental data on the activity of carbon in austenite obtained in the study of reaction (1). However, at high carbon concentrations there is a small but systematic discrepancy between the

experimentally determined values of the activity of carbon and those calculated from equation (5). In [1] these discrepancies are eliminated by introducing a small additional term proportional to the square of the carbon concentration. The activity of carbon relative to the infinitely dilute solution a_C^∞ is described by the equation

$$a_C^\infty = N_C/(1 - 5N_C) + 0.9N_C^2 \tag{6}$$

and the activity of carbon relative to graphite by

$$\lg a_C = 2105/T - 0.6735 + \lg\left(N_C/(1 - 5N_C) + 0.9N_C^2\right), \tag{7}$$

where the first two terms of the right-hand side correspond to the activity of carbon in an infinitely dilute solution relative to graphite.

In [1] the physical meaning of the correction introduced is not explained, and it is only noted that the crystallographic conditions are apparently not entirely exactly satisfied and that the number of sites for carbon is closer to 1/4.5 than to 1/4 of the number of iron atoms. In [9] it was not substantiated why precisely 1/4 of all octahedral voids can be occupied by carbon atoms, which gave grounds for considering equation (5) as empirical [4], and in this connection attempts were made to give a more accurate description of the experimental data by empirical selection of the number of sites that carbon can occupy. In [10, 11] it was concluded that the experimental data are best described if it is assumed that carbon atoms occupy 1/5

of all possible octahedral voids in the austenite lattice. Such an empirical approach is essentially devoid of physical meaning and does not make it possible to establish a connection between the thermodynamic properties of austenite and its structure.

To clarify the physical meaning of equation (7), it is useful to consider the structure of austenite on the basis of the so-called polyhedron method, proposed by L. Pauling [12] for the consideration of crystal structures. According to this method, the structure of a crystal can be regarded as consisting of polyhedra (tetrahedra, octahedra, or cubes), at whose vertices there are anions and at whose centers there are cations, usually of smaller size.

Different structures of ionic crystals can be obtained by one or another combination of polyhedra with different numbers of common corners, edges, or faces and with a definite alternation of polyhedra, at whose centers there are cations and "voids." The polyhedron method was developed by N. V. Belov [13] and made it possible to systematize a large number of crystal structures. N. V. Belov pointed out that Pauling' s method is applicable not only to ionic crystals but also to metallic phases and, in particular, to interstitial phases. In this case, metal atoms are located at the vertices of the polyhedra, while atoms of hydrogen, boron, carbon, or nitrogen may be located at the centers.

Following the polyhedron method, the structure of austenite can be represented as consisting of octahedra and tetrahedra, at whose vertices iron atoms are arranged. Carbon atoms may be located at the centers of the octahedra. Each such octahedron is connected with 12 other octahedra through common edges and with 6 octahedra through common vertices. The total number of such octahedra in the austenite structure is equal to the number of iron atoms. According to Pauling' s third rule [(12)], the presence of common edges in polyhedra lowers the stability of the structure. Let us assume, in accordance with this, that carbon atoms can be located only in octahedra having common vertices, and cannot be located in neighboring octahedra having common edges. A simple calculation shows that the number of octahedra connected through vertices is 1/4 of the total number. Thus, the physical meaning becomes clear of the assumption, made in deriving equation (5), that carbon can occupy only 1/4 of the crystallographically equivalent sites.

The fact that carbon cannot be located in neighboring octahedra having common edges is evidently connected with the strong repulsion of carbon atoms from one another in the austenite lattice. It may be assumed that repulsive forces also appear in the case when carbon atoms occupy octahedra having common vertices. The influence of the repulsion of carbon atoms occupying octahedra with common vertices can be taken into account in the following way. Let ε_0 denote the change in the solution energy upon the introduction of a carbon atom into an octahedron whose vertices are connected only with unfilled octahedra; ε_1, the change in the solution energy upon the introduction of a carbon atom into an octahedron all of whose vertices are connected with filled octahedra; and $\varepsilon_0/6$ and $\varepsilon_1/6$, the fractions of energy falling on the bond with one vertex. Then the total change in energy upon formation of the solution will be the sum of the products of the corresponding energy fractions by the number of bonds of the given type,

$$\Delta E = h_0\varepsilon_0/6 + h_1\varepsilon_1/6, \tag{8}$$

where h_0 and h_1 are the numbers of bonds with unoccupied and occupied octahedra, respectively. We shall assume the numbers of bonds of both types to be proportional to the fraction of occupied and unoccupied octahedra out of the total number, equal to 1/4 the number of iron atoms. The number of occupied octahedra is equal to the number of carbon atoms n_C, and the number of unoccupied ones is $1/4\,n_{\mathrm{Fe}} - n_C$. Then

$$h_0 = 6n_C(1/4n_{\mathrm{Fe}} - n_C)/1/4n_{\mathrm{Fe}}; \qquad h_1 = 6(n_C/2)(n_C/1/4n_{\mathrm{Fe}}). \tag{9}$$

After substituting (9) into (8) and differentiating with respect to n_C in order to obtain the partial molar energy of carbon in the solution, we have

$$\Delta\overline{E} = \varepsilon_0 + 4(\varepsilon_1 - 2\varepsilon_0)\frac{N_C}{1 - N_C}. \tag{10}$$

The change in entropy of the solution may consist of changes in the vibrational and configurational components, ΔS_{vibr} and ΔS_{conf}. Let us assume that the change in the vibrational component of the entropy is proportional to the number of dissolved carbon atoms, and calculate the configurational component of the entropy by Boltzmann' s formula

$$\Delta S = n_C \Delta S_{\text{vibr}} + k \ln W, \tag{11}$$

where W is the number of possible states, determined by relation (4) [9]. After transformation and differentiation with respect to n_C, we obtain

$$\Delta\overline{S} = \Delta S_{\text{vibr}} - R \ln N_C/(1 - 5N_C). \tag{12}$$

The chemical potential of carbon dissolved in austenite is

$$\mu_C = \Delta\overline{E} - T\Delta\overline{S} = RT \ln a_C. \tag{13}$$

Substituting (10) and (12) into (13), we obtain

$$\ln a_C = \frac{E_0}{RT} + \frac{\Delta S_{\text{vibr}}}{R} +$$

$$+\frac{4(E_1 - 2E_0)}{RT}\frac{N_C}{1 - N_C} + \ln\frac{N_C}{1 - 5N_C}. \tag{14}$$

Fig. 1. Dependences of the activity of carbon in austenite on concentration for 800° (1) and 1000° (2), calculated from equation (15). Experimental points: *a* –from [1], *b*–from [2].

Comparison of (14) with the experimental data for reaction (1) from [1,2] makes it possible to calculate the parameters E_0, $4(E_1 - 2E_0)$, and ΔS_{vibr}, and finally:

$$\lg a_C = \frac{2105}{T} - 0.6735 + \frac{317}{T}\frac{N_C}{1 - N_C} + \lg\frac{N_C}{1 - 5N_C}. \tag{15}$$

Fig. 1 shows the agreement of the experimental data with equation (15), which confirms the assumptions made about the interaction of carbon atoms in the austenite lattice.

Thus, Pauling' s polyhedron method makes it possible to establish a direct connection between the structure of austenite and its thermodynamic properties.

It should be noted that, apparently, the development of this method for analyzing interstitial structures—carbides, nitrides, borides, etc.—and comparison with the available thermodynamic data on them may substantially broaden our understanding of the nature of these compounds and of the processes occurring in them.

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Note: Figure translations are in progress. See original paper for figures.