ON THE THERMODYNAMICS OF THE REACTION OF DEPHOSPHORIZATION OF IRON

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Abstract

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A large number of works have been devoted to the study of the distribution of phosphorus in the metal–slag system ([1]-[4]). However, owing to experimental difficulties, accurate values of the thermodynamic functions of the reaction of dephosphorization of iron by slags of various compositions have not been obtained.

In the present work a new method has been applied for investigating the equilibrium of phosphorus distribution ([5]), the idea of which consists in the successive saturation of the metal, at constant temperature, with radioactive phosphorus introduced beforehand into the slag. This method makes it possible, from the temperature dependence of the phosphorus distribution index L_p, to calculate the magnitudes of both the heat effect and the entropy of the dephosphorization reaction for a slag of a definite composition.

Under any assumptions concerning the molecular composition of the molten slag, the equilibrium constant of the reaction

$$\mathrm{P} + {}^5\!/_2\mathrm{Fe}^{++} + 4\mathrm{O}^{--} \rightleftarrows \mathrm{PO}_4^{---} + {}^5\!/_2\mathrm{Fe} \tag{1}$$

may be represented in the general form:

$$K_a = L_p \varphi\left(\sum C_i\right) f\left(\sum \gamma_i\right), \tag{2}$$

where $\varphi\left(\sum C_i\right)$ is the ratio of the equilibrium concentrations of the participants in the reaction, except phosphorus; $f\left(\sum \gamma_i\right)$ is the ratio of the activity coefficients of all participants in the reaction. The form of these functions is unknown. However, under the experimental conditions, $\varphi\left(\sum C_i\right)$ does not depend on temperature. Therefore

$$\frac{d \ln K_a}{dT} = \frac{d \ln L_p}{dT} + \frac{d \ln \left(\sum \gamma_i\right)}{dT}, \tag{3}$$

Fig. 1. Schematic of the apparatus

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whence

$$\frac{d\ln L_p}{dT} = \frac{\Delta H^0 - \sum \Delta H_{\text{mix}}}{RT^2} = \frac{\Delta H}{RT^2}. \tag{4}$$

The quantity ΔH, determined from the equation

$$\lg L_p = -\frac{\Delta H}{4.573\,T} + B, \tag{5}$$

is the sum of the heat of reaction ΔH^0 between pure substances and the heats of mixing $\sum \Delta H_{\text{mix}}$.

As the standard state, 1% solutions of phosphorus in the metal and slag are taken. Then the quantity $B = \Delta S^0/4.573$, where ΔS^0 is the entropy change on transferring phosphorus from a 1% solution in iron to a 1% solution in slag. The quantities ΔH and ΔS^0 depend on the composition of the slag.

The experimental melts were carried out in an induction furnace in an apparatus whose scheme is shown in Fig. 1. About 50 g of electrolytic

iron was placed in a magnesite crucible 1, which was fixed in a beaker 3 with a magnesite packing 2. Through a quartz tube 4 in a metal water-cooled hood 5, purified nitrogen was supplied, and by means of a prism 6 the temperature of the molten iron was measured with an MOPT-48 optical pyrometer. Onto the surface of the molten iron 8, at constant temperature, a slag containing radioactive phosphorus P^{32} was fed through a funnel 9. The slag melted rapidly and passed through the walls of crucible 1 into the packing. At the same time, a certain amount of P^{32} passed from the slag into the iron. Attainment of equilibrium in the phosphorus distribution was judged from the constancy of the activity in 3-4 metal samples taken by suction into a quartz tube 10 of 2 mm diameter.

Fig. 1. Schematic of the apparatus

The value L_P was calculated as the ratio of the counting rates of slag powders and metal samples from “thin layers.” The error in determining L_P was $\pm 1.8\%$, and that in ΔH, $\pm 2.7\%$. The experiments were carried out in the temperature range 1560-1810°.

As the simplest standard system, ferrous slag was chosen, into which cations, introduced in the form of oxides and differing considerably in ionic radius, were added: Ca^{++}, Sr^{++}, and Ba^{++}.

Fig. 2. Dependence of ΔH of the dephosphorization reaction on additions of CaO, SrO, and BaO to ferrous slag and of SiO_2, P_2O_5, and Al_2O_3 to ferrous-calcium slag

Figure 2: Fig. 2. Dependence of ΔH of the dephosphorization reaction on additions of CaO, SrO, and BaO to ferrous slag and of SiO_2, P_2O_5, and Al_2O_3 to ferrous-calcium slag

The data obtained on the distribution of phosphorus between iron and ferrous slag are described by the equation

$$\lg L_P = \frac{10900}{T} - 6.41, \tag{6}$$

whence the value of ΔH is equal to -50000 cal/g-at. In this case

$$K_a = AL_P \frac{\gamma_{PO4^{-3}}}{\gamma_P}, \tag{7}$$

where A is the conversion coefficient from weight percent to mole fractions.

Fig. 2. Dependence of ΔH of the dephosphorization reaction on additions of CaO, SrO, and BaO to ferrous slag and of SiO_2, P_2O_5, and Al_2O_3 to ferrous-calcium slag

From the temperature dependence of K_a we find

$$\Delta H^0 = \Delta H + \Delta H_{\text{mix}}^{PO_4^{-3}} - \Delta H_{\text{mix}}^{P}. \tag{8}$$

For slags of more complex composition, $\Delta H_{\text{mix}}^{P}$ remains unchanged, since the solution of phosphorus in iron at low concentrations is ⋯

ideal dilute. Therefore, changes in the value of ΔH, determined for slags of more complex composition, reflect only changes in the heats of mixing of P_2O_5 with the slag melt.

The cations Ca^{++}, as well as Sr^{++} and Ba^{++}, which have larger radii than Fe^{++}, increase the heat of reaction (1) by 14,000 and 9,000 cal/g-at, respectively (Fig. 2). This does not confirm the assumptions concerning the formation of phosphates of Ca, Sr, and Ba during dephosphorization, but rather indicates an increase in the stability of the PO_4^{-3} ion. Gradual replacement of the positions of Fe^{++} in the coordination sphere of PO_4^{-3} by Ca^{++}, Sr^{++}, or Ba^{++} is possible up to a certain limit, after which its composition remains constant. In this case the ΔH of reaction (1), gradually increasing, having reached a certain value, likewise no longer changes.

Fig. 3. Effect of additions of CaO, SrO, and BaO to ferrous slag on the change in entropy of the dephosphorization reaction

Fig. 3

Figure 3: Fig. 3

The maximum value of the thermal effect of reaction (1) is observed for FeO—CaO melts. The absence of an increase in ΔH when CaO is replaced by SrO or BaO can be explained by the following assumptions. In the series Fe^{++}, Ca^{++}, owing to a definite ratio of radii, one should expect "closed" quasi-crystalline structures in the microregions of the slag melt containing phosphate ion (^{6}). Similar structures are observed in crystals with a cubic lattice when the ratio $R_{\mathrm{cation}}/R_{\mathrm{anion}}$ is less than 0.414 (^{6}). In the series under consideration it is less than 0.39 and is, respectively,
$R_{\mathrm{Fe}^{++}}/R_{\mathrm{PO4}^{-3}} = 0.303$ and $R_{\mathrm{Ca}^{++}}/R_{\mathrm{PO4}^{-3}} = 0.387$. In the presence of a "closed" structure, weakening of the electrostatic force of the cations leads to strengthening of the covalent P—O bond in the phosphate ion, which is the cause of the increase in ΔH of reaction (1).

When cations Sr^{++} and Ba^{++}, larger than Ca^{++}, are introduced into ferrous slag, the quasi-crystalline structures of the indicated microregions of the melt apparently break up, since the ratios $R_{\mathrm{cation}}/R_{\mathrm{anion}}$ in this case exceed 0.414 and are 0.465 and 0.523. As a result, cation–cation and anion–anion repulsive forces arise in the melt, increasing the energy of the melt and thereby compensating the energy gain upon interaction of the relatively weak cations Sr^{++} and Ba^{++} with anions.

It has been found that increasing the concentration of CaO or SrO and BaO in ferrous slag leads to a monotonic increase in the entropy of reaction (1) (Fig. 3). At the same time, with increasing cation radii in the series Fe^{++}, Ca^{++}, Sr^{++}, Ba^{++}, the entropy of reaction (1) increases, which corresponds to loosening of the "structure" of the slag melt, i.e., to an increase in the "free volume" in which the relatively large PO_4^{-3} ions can be accommodated. Analysis of the experimental data also shows that, at equal molar concentrations of CaO, SrO, and BaO in ferrous slag, the dephosphorizing ability of these oxides increases with increasing cation radius.

The quantitative influence of CaO on L_P can be expressed by an equation valid for $N_{\mathrm{Ca}^{++}}$ greater than 0.18,

$$\lg L_P = \frac{14\,000}{T} - 6.41 + 2.5 N_{\mathrm{Ca}^{++}}, \tag{9}$$

where $N_{\mathrm{Ca}^{++}}$ is the ionic fraction of calcium (according to M. I. Temkin (7)); 6.41 is the entropy term of equation (6).

Thus, the cations Ca^{++}, Sr^{++}, Ba^{++} promote dephosphorization both by increasing ΔH and by increasing ΔS^0. However, for the relatively weak cations Sr^{++} and Ba^{++}, the influence of the entropy factor in comparison with the energy factor is more significant than for the stronger cation Ca^{++}.

Acidic oxides SiO_2 and P_2O_5 exert a substantial influence both on the heat effect and on the entropy of reaction (1). Additions of SiO_2, as well as P_2O_5, to slags of the FeO—CaO system at $N_{Ca^{++}} > 0.18$ lead to an increase in ΔH of the dephosphorization reaction (see Fig. 2). This may be interpreted on the assumption that the PO_4^{-3} ions formed in reaction (1) are joined in the slag either to SiO_4^{-4} and PO_4^{-3} groups, or to more complex silicon-phosphorus-oxygen complexes. The polymerization process is evidently accompanied by the liberation of heat, which is the reason for the increase in ΔH of reaction (1). Confirmation of this is the fact of a sharp decrease in the entropy of reaction (1) with an increase in the concentration of SiO_2 or P_2O_5 in FeO—CaO slags (Fig. 4).

Fig. 4. Effect of additions of SiO_2, P_2O_5, and Al_2O_3 to an iron-calcium slag on the change in the entropy of the dephosphorization reaction:

$$a\text{—}\frac{\%\,\mathrm{CaO}}{\%\,\mathrm{FeO} + \%\,\mathrm{Fe_2O_3}} = 0.4;$$

$$b\text{—}\frac{\%\,\mathrm{CaO}}{\%\,\mathrm{FeO} + \%\,\mathrm{Fe_2O_3}} = 2.05$$

It is important to note that the ratio of the energy and entropy factors of the dephosphorization reaction upon the addition of SiO_2 or P_2O_5 to FeO—CaO slags is such that, with an increase in their concentration, in the first case the value of L_P decreases, and in the second it increases.

Data on the effect of alumina show that ΔH of the dephosphorization reaction does not change when Al_2O_3 is introduced into slags of the FeO—CaO system (see Fig. 2). However, with increasing Al_2O_3 concentration, a monotonic decrease in entropy is observed, without any abrupt concentration changes (see Fig. 4). This corresponds to the weaker acidic properties of Al_2O_3 in comparison with SiO_2 and P_2O_5, and at the same time indicates that, in the melts studied, aluminum is present in anionic form.

The results of the investigation show that an important influence on the equilibrium of the dephosphorization reaction, which is anionic (8), is exerted by the entropy component of the free energy, dependent on the sizes of the charges and the mutual arrangement of ions in the slag melt.

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