

CHEMICAL EQUILIBRIUM IN Fe–O–H SYSTEM AT HIGH TEMPERATURES

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The issue of thermodynamic equilibrium in Fe–O–H system at the temperature of steel-making processes (1600 °C) was considered. The historical data array, features of experiments on obtaining them and their drawbacks were analyzed. A new more correct calculation of hydrogen and oxygen concentration in liquid iron and in the gas phase was performed. New coefficients of activity were calculated, proceeding from precise thermodynamic principles, unlike the earlier used artificial models based on interaction parameters. 19 Ref., 6 Figures.

Keywords: thermodynamics; iron; hydrogen; oxygen; solutions; activity; equilibrium

Interaction in Fe–O–H system, together with Fe–O–C system, is fundamental in steel production [1–3]. This system has been studied in great detail for the conditions of reduction of iron oxides in the solid phase and in less detail for interaction of liquid iron with the gas phase. In the latter case, most of the known fundamental studies were focused either on determination of hydrogen solubility in liquid iron, or of oxygen solubility, using a gas mixture of H₂O–H₂ [3]. Despite the importance of the data on interaction in this system, in publications there is practically no detailed diagram of phase equilibrium at high temperatures (for instance, 1600 °C) or any consistent data on hydrogen or oxygen activities, when they are simultaneously present in liquid iron. The majority of these data (obtained in the previous century) use artificial simplified models of the solutions with application of interaction parameters, which do not have an appropriate and substantiated thermodynamic base [2–4]. The differences in previous experiments and the then applied analytical methods do not allow plotting the respective phase diagrams, based on such data.

In order to develop a thermodynamically substantiated approach to equilibrium in this system, in this work the available data on hydrogen and oxygen concentration in liquid iron were analyzed, and new calculations were performed and respective diagrams were plotted.

Known experimental data. One of the first studies of hydrogen and oxygen solubility in iron were the works by Hamilton and Vacher [5, 6]. They used a gas-vapour mixture of H₂O–H₂ as an auxiliary sub-

stance to study oxygen solubility in parallel with investigations of Fe–O–C system equilibrium. They also took the first measurements of hydrogen content and came to the conclusion that its quantity is quite insignificant, and has no influence on oxygen content. Compared to measurements taken 30–40 years later, it is clear that in these experiments [5, 6] the exact hydrogen content could not be measured, using the methods available in those times.

Development of the theory and technology of steel production was accompanied by a series of investigations of hydrogen and oxygen solubility, due to higher requirements made of the steel quality [2], in particular, for railway transport [7]. More detailed measurements at that time, taken at different temperatures, and, what is important, at different argon and hydrogen ratios in H₂O–H₂–Ar gas phase, are given in work [8]. They determined the formal constant of equilibrium of the following reaction



showing that it is not steady, but depends on H₂O/H₂ and Ar/H₂ ratio [8]. However, the researchers did not pay enough attention to the question of how exactly does the Ar/H₂ ratio influence either the equilibrium of reaction (1), or hydrogen solubility in iron.

In a parallel study [9], the authors noted the influence of Ar/H₂ ratio not only on hydrogen content, but also on oxygen concentration, even though in the conditions of a limited concentration range. In work [10], the authors added more experimental points in this system at higher values of H₂O/H₂ ratio at Ar/H₂ = 5. Later on in work [11] the limit of hydrogen sol-

ubility in liquid iron was determined at 1600 °C in 25.9 ppm (or 10⁻⁴ %) or in 0.00142 mole fractions, if iron is in equilibrium with pure hydrogen at the pressure of 1 Atm.

In work [12] the authors noted the fact that it is incorrect to consider the thermodynamics of just reaction (1), ignoring hydrogen solubility in iron, simultaneously with oxygen, even if its concentration is low. They synchronously analyzed the content of hydrogen and oxygen in iron in equilibrium with H₂O–H₂ gas phase, but without argon additives (Ar/H₂ = 0). Figure 1 shows the results of these and other experimental measurements. As one can see from this data, in the experiments in [8] hydrogen concentration in the solution was practically unchanged, despite the variation of partial pressure of water vapour. This does not agree well with other independent data [9, 10, 12], possibly because in work [8], the Ar/H₂ ratio was not kept constant.

Despite all these works, a very simplified approach, based solely on reaction (1) almost without exception, predominated in the theory of steel-melting processes [1, 13] for a long time. In work [4] it is shown that such an approach is incorrect from the viewpoint of the rule of phases, as it ignores the presence of other components in the system. Application of a similar approach to Fe–O–C system showed that taking into account CO₂ and CO simultaneously much better agrees with the experiments, than when it is just CO. It is worth noting that the need to measure CO₂ alongside CO, was shown already in 1930s [5, 6], but this fact was not considered any further in terms of the process thermodynamics.

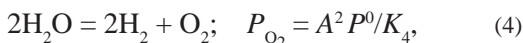
Formalism of equilibrium in Fe–O–H–Ar system. Available results can be first described by the balance of masses. We will assume that all the main components of the gas phase are ideal:

$$P_{H_2} + P_{H_2O} + P_{O_2} + P_{Ar} = P^0, \quad (2)$$

where P^0 is the total pressure (1 atm). Introducing designations $A = P_{H_2O}/P_{H_2}$, $B = P_{Ar}/P_{H_2}$, we can write (2) as follows:

$$P_{H_2} (1 + A + B) = P^0 - P_{O_2}. \quad (3)$$

As at high temperatures the equilibrium in the gas phase is practically instantaneous, the partial pressure of oxygen can be determined through the constant of the reaction of water vapour dissociation:



which has been assessed in detail many times. At 1600 °C by the data of [1, 12] $\lg K_4 = 8.000-8.0827$, and by the new data $\lg K_4 = 7.97161$ (thermodynamic data base «FactSage 8.0», 2020). Thus, the partial

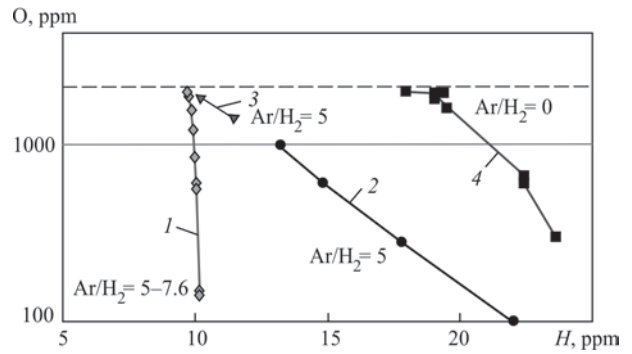


Figure 1. Experimental data (1 — [8]; 2 — [9]; 3 — [10]; 4 — [12]) on oxygen and hydrogen content in liquid iron at 1600 °C. Horizontal line shows the limit of oxygen solubility

pressure of hydrogen and oxygen in any mixture will be defined as follows:

$$\begin{aligned} P_{H_2} &= P^0 (1 - A^2/K_4)/(1 + A + B); \\ P_{O_2} &= A^2 P^0 / K_4. \end{aligned} \quad (5)$$

An interesting conclusion can be made from formula (5): partial pressure of oxygen does not depend on B (Ar/H₂ ratio), unlike partial pressure of hydrogen, which depends both on Ar/H₂ and on H₂O/H₂. It accounts for the discrepancies (Figure 1) in the experimental results with argon application.

Hydrogen and oxygen in the gas phase interact with liquid iron in proportion to their concentrations, forming Fe–[H]–[O] solution. In this case we assume that Ar does not dissolve in liquid iron, and then the content of hydrogen and oxygen will be proportional to activities of these components in equilibrium with partial pressures of hydrogen and oxygen. The component activity (or coefficient of activity (γ_i)) is a measure of effectiveness in a particular solution in terms of its reactions with other components. A classical definition of the activity links it with partial pressure of the dissolved component in the solution relative to its reference state, as a pure substance:

$$a_i(X_i) = P_i(X_i) / P_i^0, \quad (6)$$

where P_i is the partial pressure of this component; P_i^0 is its pressure in the reference state ($a_i^0 = 1$). Many thermodynamic calculations take a default reference state, designed for a pure substance. However, for a metallurgical system at 1600 °C, the pure liquid oxygen is not a reference state, as it cannot exist in such a form. It was shown [16, 17] that such hypothetical reference states, which earlier were used in metallurgical practice for years, lack thermodynamic and mathematical substantiation [14]. In the thermodynamics of metallurgical processes, the Wagner–Lupis–Elliott formalism was traditionally used with expansion of the coefficient of activity into the Taylor series [3, 4, 14], when the reference state was selected to be the

formal composition of the solution with 1 wt.% of the component (even if such a solution did not actually exist). However, the Taylor series expansion is only valid around a point, where the derivative with respect to concentration is taken [17], and it cannot be extrapolated on the whole to a wide concentration range. Work [18] showed that the traditional Wagner–Lupis–Elliott equations are invalid with respect to the basic Gibbs–Duhem equation [19]. The authors of [17] showed the five main principles for correct selection of the reference state and calculation of the chemical potential, and proved that the reference state of a component in a solution is its solubility limit under

these conditions, as all the required thermodynamic and mathematical conditions are fulfilled only there.

Thus, for hydrogen the reference state at 1600 °C is in place at its maximum content in iron (25.9 ppm) at equilibrium with pure hydrogen at the pressure of 1 atm [11], while the reference state for oxygen (maximum oxygen content of approximately 0.20 %) is observed at equilibrium with such a gas mixture, for which the partial pressure of oxygen reaches $5.11 \cdot 10^{-9}$ atm (contact with pure oxygen would have led to complete transformation of iron into oxides). These maximum concentrations correspond to activities, equal to 1 for hydrogen and oxygen, as:

- Gibb’s energy function is continuous and differentiated by the quantity of substance added to the solution phase, when this solution is present (is not hypothetical);
- component activities are real, measurable and continuous, monotonically growing functions in the solution phase (saturation state is reached within the appropriate concentration range);
- in the saturated state the derivatives for component activity by temperature and by pressure are zero.

Correct determination of the activities and free energy enable calculating the detailed equilibrium in Fe–O–H system.

Numerical thermodynamic calculation in Fe–O–H system. Thermodynamic calculation will be performed, using «FactSage 8.0» software and data bases. The formal diagram of phase equilibrium in this system at 1600 °C was first calculated in mole fractions (Figure 2). One can see two phase regions from the iron side: metal-gas or metal-gas-slag (liquid iron oxides). If oxygen content is not high, and that of hydrogen is practically absent, then the third possible phase (iron-slag) can be in equilibrium with iron without any evident gas phase (Figure 2, b). The same diagram was calculated in weight percent (Figure 3). One can see that the line of equilibrium between slag (FeO) and liquid iron is almost horizontal, that points to practically unchanged oxygen solubility limit, despite an increase of hydrogen content to a concentration of approximately 0.0019 % [H]. Further increase of hydrogen in the system leads to an abrupt drop of oxygen content in iron.

The next calculation was made for the case of added argon at $Ar/H_2 \approx 0.1–0.2$ and 5.0–6.0 under other conditions being equal (Figure 4). As argon concentration has little influence on oxygen content, the dependence of hydrogen content on Ar/H_2 was assessed at different H_2O/H_2 (Figure 5).

This hydrogen content can be approximated by a regression equation in Figure 5, which predicts hydrogen concentration the more accurately, the higher

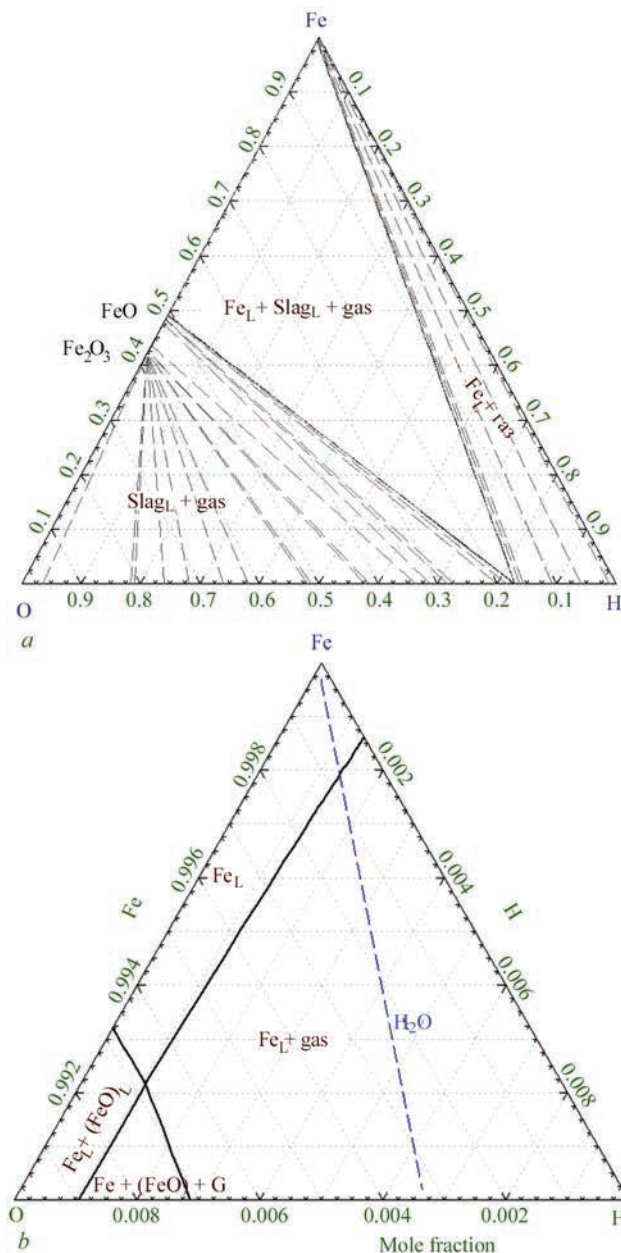


Figure 2. Diagram of phase equilibrium in Fe–O–H system at 1600 °C (a) and angle from the iron side, as component (b), using correct chemical potentials [17]. Dash line determines the stoichiometry of water vapour (mole ratio of hydrogen to oxygen is equal to 2)

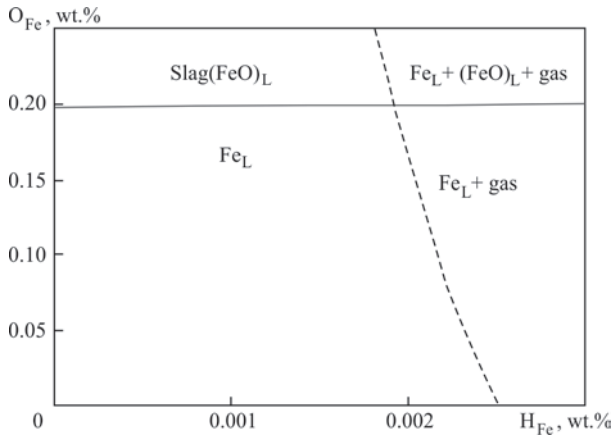


Figure 3. Phase equilibrium diagram in Fe–O–H system at 1600 °C. Regions of stability of different phases are shown

is $B = \text{Ar}/\text{H}_2$ ratio. It is logical, as at low argon content ($B \rightarrow 0$) the quantity of hydrogen in the solution will strongly depend on $A = \text{H}_2\text{O}/\text{H}_2$ (by expression (5)). At B increase, particularly at $B > A$ the hydrogen content will be mostly determined exactly by Ar/H_2 ratio (it is rational to note that at 1600 °C the maximum value of $A < 0.5\text{--}0.75$, when iron oxides, i.e. slag, still do not form). In previous experiments (see Figure 1) using argon, the values of $B = 5.0\text{--}7.6$, that also accounts for considerable differences in the measured hydrogen concentrations at similar $\text{H}_2\text{O}/\text{H}_2$ values.

The next question was determination of the coefficients of hydrogen and oxygen activity in the solution. The direct approach uses the ratio of component activity to its concentration in mole fractions and does not require any artificial models of the solutions [12, 14, 16, 17]. In keeping with equation (6) in the reference state ($a_i = 1$), the coefficient of activity of any component (γ_i^0), which will be equal to its reverse saturated concentration (X_i^0):

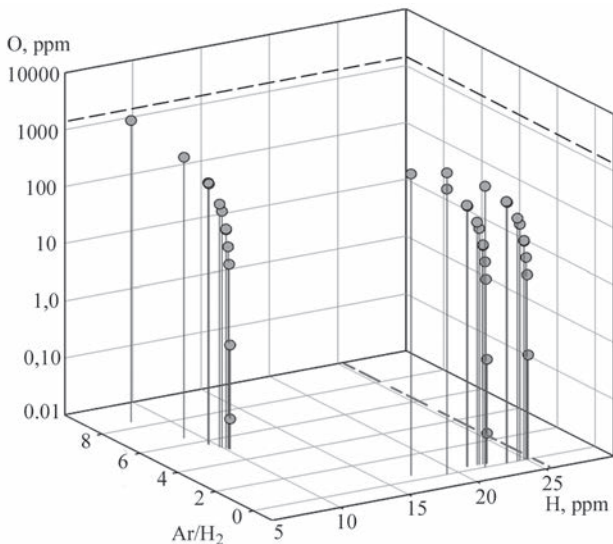


Figure 4. Oxygen and hydrogen content in Fe–O–H system at 1600 °C for different Ar/H_2 ratios. Dash lines show the solubility limits of hydrogen and oxygen

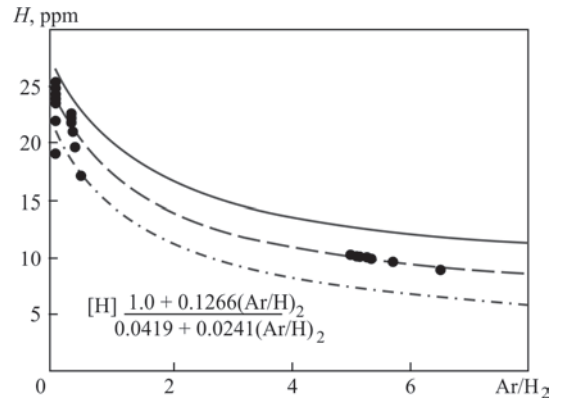


Figure 5. Hydrogen content in Fe–O–H system at 1600 °C (Figure 4) for different Ar/H_2 ratios. Dash lines show the confidence interval for the regression equation

$$\gamma_i^0 = 1/X_i^0 \tag{7}$$

Coefficients of activity of hydrogen and oxygen change, depending on Ar/H_2 and $\text{H}_2\text{O}/\text{H}_2$ ratios within narrow limits, but nonlinearly (Figure 6). The first ratio has a stronger impact on the coefficient of oxygen activity and much less on the coefficient of

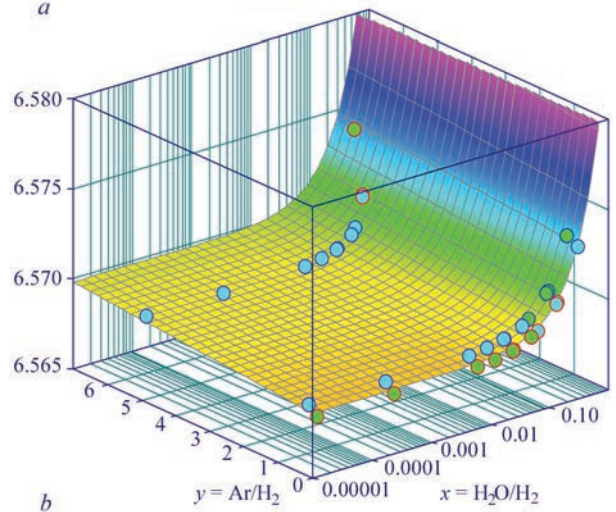
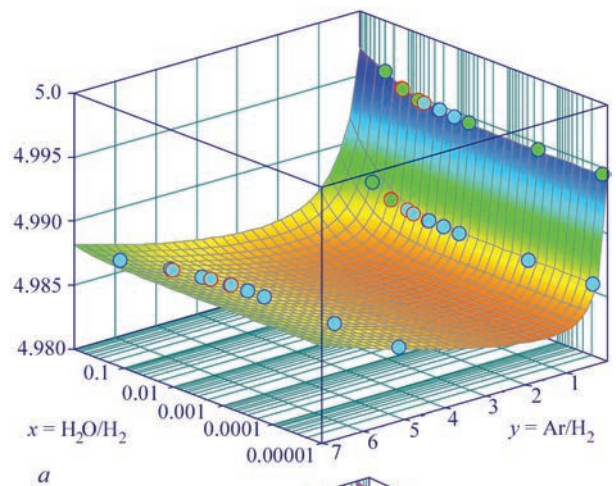


Figure 6. Natural logarithms of the coefficients of activity of oxygen $\ln(\gamma_O) = (a + bx + cy + dy^2)/(1 + ex + fy + gy^2)$: $a = 4.9944208$; $b = 11.13995$; $c = 32.451068$; $d = -0.88011301$; $e = 2.2286863$; $f = 6.515328$; $g = -0.17770942$ (a) and hydrogen $\ln(\gamma_H) = a + bx + cy$: $a = 6.5685561$; $b = 0.016389753$; $c = 0.00018215654$ (b) in liquid iron from Ar/H_2 and $\text{H}_2\text{O}/\text{H}_2$ ratios at 1600 °C

hydrogen activity. The second has an opposite effect: has a stronger influence on the coefficient of activity of hydrogen, and not oxygen, as it could have been anticipated. One can see from regression equations in Figure 6, that the influence of $y = \text{Ar}/\text{H}_2$ and $x = \text{H}_2\text{O}/\text{H}_2$ ratios on the coefficient of activity of hydrogen, is independent on the other, i.e. there is no correlation between the influence of these ratios (Figure 6, *b*). For oxygen, contrarily, the simultaneous impact of these ratios of the coefficient of activity is in place (Figure 6, *a*). Approximating the surfaces and equations, a nonlinear regression was plotted by points, calculated in this work.

Thus, we can note that hydrogen content in liquid iron, which is controlled by Ar/H_2 and $\text{H}_2\text{O}/\text{H}_2$ ratios simultaneously, influences the coefficient of activity of oxygen and its concentration stronger that it was earlier believed. A similar influence on the coefficient of activity of hydrogen is smaller, and it depends more on $\text{H}_2\text{O}/\text{H}_2$, as does hydrogen concentration at smaller Ar/H_2 values.

Conclusions

1. Analysis of the known experimental data on interaction of Fe–O–H–Ar system was performed, as well as calculations of phase equilibrium diagram, using new data, allowing for correct determination and calculation of the component activity.

2. It is shown that partial pressure of oxygen in the gas phase is independent on Ar/H_2 ratio, unlike partial pressure of hydrogen, which depends both on Ar/H_2 , and on $\text{H}_2\text{O}/\text{H}_2$. It accounts for the available discrepancies in the results of historical experiments, using argon.

3. Hydrogen content in liquid iron can be approximated by a regression equation, which predicts hydrogen concentration the more accurately, the higher is the Ar/H_2 ratio. At a low content of argon the quantity of hydrogen will strongly depend on $\text{H}_2\text{O}/\text{H}_2$, and in the opposite case the hydrogen content will be mostly determined exactly by Ar/H_2 ratio.

4. The coefficients of activity of hydrogen and oxygen change depending on Ar/H_2 and $\text{H}_2\text{O}/\text{H}_2$ ratios in narrow ranges, but nonlinearly. The first ratio has a stronger influence on the coefficient of activity of oxygen and a much weaker one on that of hydrogen. The second has an opposite effect: it influences the

coefficient of activity of hydrogen more than that of oxygen, as one might have foreseen.

5. Investigation results are of practical importance for controlling the hydrogen and oxygen content at steel treatment by argon-based gas mixtures in the presence of water vapour. This approach can be extended to alloyed steels and alloys of different composition.

1. Filippov, S.I. (1967) *Theory of metallurgical processes*. Moscow, Metallurgiya [in Russian].
2. Velichko, A.G. (2005) *Out-of-furnace steel treatment*. Dnepropetrovsk, Sistemnye Tekhnologii [in Russian].
3. Okhotsky, V.B., Kostyolov, O.L., Simonov, V.K. (1997) *Theory of metallurgical processes*. Kyiv, IZMN [in Ukrainian].
4. Knyuppel, G. (1973) *Deoxidation and vacuum treatment of steel*. Moscow, Metallurgiya [in Russian].
5. Vacher, H.C. (1933) The system liquid iron–carbon oxides. *US Bureau of Standards J. Res.*, **11**, 541–551.
6. Vacher, H.C., Hamilton, E.H. (1931) Carbon–oxygen equilibrium in liquid iron. *Transact. AIME*, **95**, 124–140.
7. Kozlovsky, A.I., Medovar, B.I., Projdak, Yu.S. et al. (1999) Application of methods of special electrometallurgy and out-of-furnace treatment in production of wheel steel. *Problemy Spets. Elektrometallurgii*, **2**, 31–38 [in Russian].
8. Sakao, H., Sano, K. (1960) Equilibrium between dissolved oxygen in liquid iron and H_2 – H_2O gas mixtures. *Transact. JIM*, **1**, 38–42.
9. Schenck, H., Wunsch, H. (1961) Über die Gleichgewichtslöslichkeit des Wasserstoffs im flüssigen reinen Nickel und Eisen und die Beeinflussung im Eisen durch Sauerstoff. *Arch. Eisenhüttenw.*, **32**(11), 779–790.
10. Gasik, M.I., Khitrik, S.I. (1965) Interaction of liquid iron with vapor-hydrogen mixture. *Metallurgiya i Koksokhimiya*, **3**, 5–16 [in Russian].
11. Ban-ya, S., Fuwa, T., Ono, K. (1967) Solubility of hydrogen in liquid iron alloys. *Tetsu-to-Hagane*, **53**, 13–28.
12. Kubaschewski, O., Alcock, C.B. (1979) *Metallurgical thermochemistry*. 5th Ed. Pergamon Press, Oxford.
13. Sanbongi, K. (1981) Thermodynamics of ironmaking and steelmaking processes. *Transact. JIM*, **22**, 663–676.
14. Lupis, C.H.P. (1983) *Chemical thermodynamics of materials*. North-Holland, NY.
15. Gasik, M.M., Gasik, M.I. (1985) Thermodynamic investigation of hydrogen–oxygen equilibrium in liquid iron. *Izv. AN SSSR. Metally*, **3**, 22–30 [in Russian].
16. Gasik, M. (2013) *Handbook of Ferroalloys: Theory and Technology*, Elsevier. Butterworth-Heinemann, Oxford, UK.
17. Gasik, M.M., Gasik, M.I. (2020) Chemical potentials and activities in metallurgical processes. *Suchasna Elektrometallurhiya*, **4**, 39–43 [in Ukrainian].
18. Hillert, M. (1998) *Phase equilibria, phase diagrams and phase transformations: Their thermodynamic basis*. Cambridge Univ. Press, Cambridge, UK.
19. Schuhman, R.Jr. (1955) Application of Gibbs–Duhem equations to ternary systems. *Acta Metall.*, **3**, 219–226.

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