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Corrosive behavior of low-alloy structural steels

V.G. Kiselev **,** ***A.A. Kalyutik****
Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

**E-mail: AA_Kalyutik@spbstu.ru*

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Abstract. Increasing the corrosion resistance of low-alloy steels containing less than 2.5% of doping components (except carbon), which are actively used in the construction of various buildings and structures, is one of the priorities in the development of the modern construction industry. This problem becomes especially urgent during operation of stressed elements of various structures, which are used in the conditions of possible surface exposure to moisture. As part of the research, the results of which are presented in this article, we have examined the possible reduction in the rate of electrochemical corrosion of low-alloy steels in a natural corrosive environment. The purpose of the study was to establish the effect of the composition of steels on their corrosive properties. The main method chosen was a method of thermodynamic potentials, used in conjunction with model ideas about ideal gas and free energy of diffusion of liquid, solid and gaseous solutions. The present study analyzes the process of formation of ideal binary alloy, based on which the relationship between the thermodynamic characteristics of its original components and the corrosive behavior of the alloy was established. In order to verify the detected corrosion mechanism, the process of amalgam anode dissolution was considered, which fully confirmed the results obtained earlier. Based on the analysis conducted, it can be concluded that the equilibrium potential of the ideal binary alloy in the electrolyte in no way depends on the process of its formation from the pure original components. It is determined solely by the ratio of energy characteristics of metal ions actually in the alloy, as well as the energy characteristics of the same ions in the solution of electrolyte, which comes into contact with the alloy.

1. Introduction

Buildings, with the exception of temporary ones, are designed for a very long service life in the presence of significant adverse conditions associated with simultaneous effects of various aggressive factors. Such factors include: mechanical load, solar radiation, as well as chemical, electrochemical and microbiological activity of the environment, etc. [1–4], which in turn contribute to the intensification and localization of corrosive processes that occur to varying degrees on the metal parts of almost all modern architectural objects. Hence, there is a need for long-term forecasting of the behavior of the materials used, especially metals and their alloys. A significant role in this case is played by their corrosive resistance, in the water solutions of electrolytes in particular, as that is where soil and atmospheric corrosion, characteristic of such structures, occurs.

Due to the fact that in modern industrial construction we almost always use only alloys (not pure metals), the study and prediction of their corrosive behavior is a priority for the relevant construction industry and the part of material science that serves it, as well as the study of metal corrosion, which shows the extreme relevance of this problem in the realities of today.

The main method used to solve the problem of corrosion of alloys in active state is the analysis and synthesis of methods of chemical kinetics and thermodynamics. Here the key role is played, on the one hand, by the method of thermodynamic potentials, and on the other hand, by the theory of electrochemical

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kinetics. We should note that thermodynamic research methods are in high demand today. References to them are found not only in articles in academic publications, but also in books and journals specializing in publications of pronounced applied nature. In this case, it is appropriate to recall a series of articles related to metal corrosion in electrolyte (soil) in the presence of an additional factor of aggressiveness due to the presence of an alternating stray current in the system. Thermodynamic analysis of the corrosion process of such objects is usually carried out using the Pourbaix diagrams [5–7]. The second area where thermodynamics techniques are actively used is the cathode protection of underground metal structures from corrosion [8–11]. In this case, it is appropriate to recall the technique for measuring potentials (stationary and polarization), which is based on the theory and practice of using non-polarizable reference electrodes [12], usually copper-sulfate ones.

In all these cases, kinetic methods for studying anodic dissolution of metals are also used. However, almost all of these works do not analyze the process of obtaining alloys, and, consequently, its effect on their corrosive behavior. This fact speaks about the extreme relevance of research devoted to this subject. The exception to this rule is the works of I.K. Marshakov [13]. We need to note that the traditional approach to thermodynamic analysis of corrosive behavior of alloys considers the process of their formation, primarily, as ideal solid solutions and connects this phenomenon with the corresponding change in free energy and entropy. Due to the fact that the formation of the alloy occurs spontaneously, it is automatically accepted that this event is accompanied by a decrease in Gibbs free energy (at constant pressure and temperature) of the system [13, p. 89], which, it its turn, can be transformed into the appropriate amount of electrical work described by the following formula:

$$G_i^M = \bar{G}_i - G_i^0 = RTlnN_i = -z_iFE_i^M, \tag{1}$$

where G_i^M is relative partial molar free energy of the i^{th} component; $\bar{G}_i$ is partial molar free energy of the i^{th} component; G_i^0 is molar free energy of the i^{th} component (pure matter); R is the Universal gas constant; T is absolute temperature; N_i is molar fraction of the i^{th} component in a solid solution; z_i is valence of the i^{th} component (i^{th} metal); F is the Faraday constant; E_i^M is potential difference corresponding to electrical work due to the presence of the relative partial molar free energy of the i^{th} component.

From the last formula, I.K. Marshakov [13, p. 89] has obtained the value of the partial relative electrode potential of the i^{th} component for standard conditions, namely E_i^M :

$$E_i^M = \bar{E}_i - E_i^0 = -\frac{RT}{z_iF}lnN_i, \tag{2}$$

where $\overline{E_i}$ is equilibrium partial electrode potential of the i^{th} component in the alloy, determined by the equilibrium between the component in the alloy and the ions of this component in the electrolyte solution; E_i^0 is equilibrium standard potential of the pure i^{th} component.

Since the molar (atomic) fraction $N_i < 1$, then $E_i^M > 0$ always. Thus, alloy formation leads to a shift of potential in a positive direction ($\overline{E_i} > E_i^0$). Therefore, if the anode dissolution of the alloy occurs in conditions close to equilibrium, then there should be an inhibition of the anode reaction for any component [13, p. 89]. We should note that this view is broadcast by a number of subsequent authors, for example, N.I. Isaev.

However, based on the article of one of the co-authors of this publication [14], it is possible to show some illogicality of the last thesis stated by I.K. Marshakov and supported by a number of his followers. In the last paper listed [14], on the example of the ideal gas it was shown that the mixing process (the formation of the ideal solution) is indeed accompanied by a change in Gibbs (Helmholtz) energy. However, this change in no way affects the energy state of the components of the alloy (ideal solution), in other words, the energy of the substance molecules' communication with each other is the same, both in the alloy, which is an ideal solid solution, and in the pure matter. Indeed, as it does, however, directly follow from the definition of the concept of the ideal solid solution, the following conditions should be observed in its formation:

1. When pure components are mixed, there is no change in the volume of the system;
2. The heat of the mixing is zero, i.e. there is no interaction between the components of the solution;

3. The vapors of components above the solution behave like ideal gases and at all concentrations of the solution the Raoult's law is fulfilled:

$$P_i = P_i^0 N_i, \tag{3}$$

where P_i is partial pressure of the ideal gas consisting of the i^{th} component of the alloy above its surface, and P_i^0 is pressure of the ideal gas consisting of the i^{th} component of the alloy above the surface of the alloy.

This definition is enough to show the invariability of the energy state of individual molecules in the formation of ideal solid solutions, which, however, is mentioned by I.K. Marshakov himself [13, pp. 41–44]. Moreover, in [14] this thesis is confirmed in various ways, including using the method of thermodynamic potentials. Therefore, on the basis of these data, we can state that the process of forming an ideal alloy is not accompanied by changes in the energy state of the molecules of substances involved in the process under consideration and, therefore, at least some adjustment of the formulas (1) and (2) above is necessary. Indeed, the ratio (2), due to the energy equality of molecules involved in the subsequent electrochemical process of anode dissolution of the alloy, can no longer be recognized as fair, which leads to its degeneration, which, in its turn, can be illustrated by the following:

$$E_i^M = \overline{E}_i - E_i^0 = 0. \tag{4}$$

However, the equation (1), at least, its left part, due to the spontaneity of the process of alloy formation cannot be recognized as incorrect. This circumstance automatically raises the question of the legality of its use to obtain the ratio (2). At the same time, there arises a problem of interpreting the physical meaning of the equation (1), which, in particular, is the subject of this study. In other words, the purpose of this work is to perform thermodynamic analysis of the process of binary ideal alloy formation and to establish the mechanism of its effect on electrochemical corrosive processes occurring on their surfaces.

To achieve this goal, we will have to solve the following two problems:

1. Conducting a thermodynamic analysis of the process of ideal binary alloy formation.
2. Establishing a relationship between the thermodynamic characteristics of the original components of the ideal binary alloy and its corrosive behavior.

In the following sections of this work, we will focus on solving these problems in some more detail.

2. Materials and Methods

The work uses one of the most widespread analytical methods of research in modern thermodynamics, which is called the method of thermodynamic potentials (or characteristic functions). The main advantages of this method include its suitability for analysis of non-cyclical processes, such as chemical reactions, diffusion processes, mixing processes (formation of solutions), etc. Its essence is included in almost any book on thermodynamics and lies in the fact that the basic thermodynamic equation allows for a quasi-static thermodynamic system to derive some state functions, called thermodynamic potentials, the change of which with a change in the state of the system is a complete differential. Based on this circumstance, it is possible to write down the corresponding mathematical equations suitable for describing the process under consideration, which we will demonstrate in this article.

3. Results and Discussion

3.1. The formation of the ideal solid solution

The main method that we will use to solve the problem outlined in the introduction to this article is the method of thermodynamic potentials. To simplify the analysis of the process, let us assume that our system consists of a number of ideal gases, which are to be mixed. Without loss of generality, we will assume that there are two such gases (first and second). Replacing the ideal solid solution with the ideal gas from a thermodynamic point of view is quite acceptable, as in this case all the energy characteristics of the systems under consideration are equal to each other up to a constant. This fact for the ratios aimed at studying the changes taking place in the quasi-static systems under consideration practically indicates their equivalence.

A more detailed examination of the stated thesis will be based on a specific example. For greater visibility, the analysis will be carried out using the energy characteristics of this object, which include, first of all, the free energies of Gibbs and Helmholtz. In addition, without loss of generality, let us accept that the volume in which each of the two types of ideal gas to be mixed is originally located, is V_1 and V_2 accordingly, and the total volume of the mixture, after their mixing is equal to $V = V_1 + V_2 = 1$. However, the invariance of the initial pressure P during mixing of two potions of ideal gases (identical or different) directly follows from the thermal equation of the state of ideal gases [14].

Of course, the stated thesis is valid only if the mixture is still an ideal gas and the number of molecules in it remains the same. After the introductory remarks have been made, we proceed to a direct examination of the process of combining two generally different portions of different ideal gases.

3.2. Mixing two portions of different ideal gases

We will briefly return again to the system consisting of two generally different portions of different first and second ideal gases, placed in two volumes, V_1 and V_2 respectively, so that the following ratio is observed: $V = V_1 + V_2 = 1$. At the same time, between them there is some partition, which can be removed, and ideal gases differ from each other, for example, there can be a small difference in the size of molecules. When this partition is removed, they are mixed in the volume V. Let us assume that the total amount of first and second gases is equal to one mole, i.e. in other words, the following ratio is observed:

$$G_m = N_1\overline{G_1} + N_2\overline{G_2}\ , \tag{5}$$

where G_m is the Gibbs molar energy of the mixture of the ideal gases; $\overline{G_1}$ and $\overline{G_2}$ are the partial Gibbs molar free energies, respectively, of the 1st and 2nd components of the mixture of two ideal gases; N_1 and N_2 are molar fractions of the 1st and 2nd components in a mixture of two ideal gases.

In addition, it is clear that, according to the conditions imposed, the following ratios must be satisfied:

$$N_1 = \frac{n_1}{n_1 + n_2}, \tag{6}$$

$$N_2 = \frac{n_2}{n_1 + n_2}, \tag{7}$$

$$n_1 + n_2 = 1, \tag{8}$$

where n_1 and n_2 are the number of moles of the 1st and 2nd components in the mixture of two ideal gases.

We need to note that if the last ratio is satisfied, the following is also true: $N_1 = n_1$ and $N_2 = n_2$. When two identical ideal gases are mixed, there is no change in any macroscopic parameters of the system, namely temperature, pressure and its total volume remain unchanged. In this case, for the Gibbs free energy of the combined system [14], we can write the following ratio:

$$G_m = G_1 + G_2, \tag{9}$$

where G_1 and G_2 are the Gibbs free energies of the 1st and 2nd initial components of the two ideal gases.

Therefore, based on the latest formula, the change in the Gibbs free energy ΔG when mixing two portions of the same ideal gas, provided the gas mixture is also ideal, will be equal to:

$$\Delta G = G_m - G_1 - G_2 = 0\,. \tag{10}$$

However, in the system under consideration, consisting of n_1 and n_2 moles of two different ideal gases located in two generally not in equal volumes, divided by an impenetrable partition, there is, at least still one more energy component. It is the of Gibbs free energy of diffusion inherent in this system as a whole. Its very existence in this case is inextricably linked to the fact that our object has some practical or theoretical possibility of mixing existing different ideal gases. This mixing can occur in equilibrium (getting third-party work using semi-permeable membranes) or nonequilibrium (removal of an impenetrable partition between the two ideal gases) ways.

In this case, it is appropriate to recall the monograph of L.I. Antropov, in which he during thermodynamic analysis of the properties of ideal and real solutions in particular considered the behavior of the diffusion component of the Gibbs free energy. The fact that is relevant for us is that in his work he used a differential from the Gibbs free energy of diffusion G, which was defined by him as follows:

$$dG = \sum_i n_i d\mu_i, \tag{11}$$

where n_i is the number of moles of the *i*th substance participating in the process, and μ_i is the chemical potential of this *i*th substance.

In the case of one mole of the *i*th ideal gas, its Gibbs energy G_i, equal to its chemical potential μ_i, as we know [13, p. 20], equals:

$$G_i = G_i^0 + RT\, lnP_i, \tag{12}$$

where G_i^0 is the standard Gibbs energy value equal to a constant.

If there are two different ideal gases, based on the previous ratio, the equation (11) can be rewritten as follows:

$$dG = RT\sum_{i=1}^{2} n_i d(lnP_i). \tag{13}$$

After differentiation and trivial transformation of the right part of the last ratio, we get

$$dG = n_1 RT\frac{dP_1}{P_1} + n_2 RT\frac{dP_2}{P_2}. \tag{14}$$

At the same time, the Gibbs free energy of the original state of the system under consideration G_n is known to be an additive function of its constituent subsystems, namely:

$$G_n = G_{1n} + G_{2n}, \tag{15}$$

where G_{1n} and G_{2n} are, respectively, the Gibbs initial free energies of the first and second ideal gas, which in turn are determined by the following ratios [13, p. 20]:

$$G_{1n} = n_1(G_1^0 + RTlnP_{1n}), \tag{16}$$

$$G_{2n} = n_2(G_2^0 + RTlnP_{2n}), \tag{17}$$

where G_1^0 and G_2^0 are, accordingly, the standard values of Gibbs initial free energies of the first and second ideal gases, which are known to be constant, but in general are not equal to each other, which is confirmed by the presence of at least different values of heat capacities of different ideal gases; P_{1n} and P_{2n} are, respectively, the initial pressures of the first and second ideal gases initially located in volumes V_1 and V_2.

We will mix two original portions of ideal gases while maintaining the total volume of the system $V = 1$. In this case, the final free energy of each of these gases, G_{1k} and G_{2k}, by reducing their partial pressures and lack of interaction between them, will be characterized by the following values of Gibbs energy:

$$G_{1k} = n_1(G_1^0 + RTlnP_{1k}), \tag{18}$$

$$G_{2k} = n_2(G_2^0 + RTlnP_{2k}), \tag{19}$$

where P_{1k} and P_{2k} are, respectively, the partial pressures of the first and second ideal gases after they mix in the volume $V = 1$.

Now we will determine the values P_{1n} and P_{2n}, as well as P_{1k} and P_{2k}. To do this, we will use thermal equations of the state of the ideal gas

$$PV = nRT \,, \tag{20}$$

where n is the number of moles of the ideal gas.

The last ratio for the first and second ideal gas taking part in the mixing process, characterizing their initial state in the system, can be rewritten in the following form:

$$P_{1n}\ V_1 = n_1RT \,, \tag{21}$$

$$P_{2n}\ V_2 = n_2RT \,, \tag{22}$$

where P_{1n} and P_{2n} are initial pressures of the first and second ideal gas respectively.

In this case, for the characteristics P_{1n} and P_{2n}, we obtain:

$$P_{1n} = RT\frac{n_1}{V_1} \,, \tag{23}$$

$$P_{2n} = RT\frac{n_2}{V_2} \,. \tag{24}$$

The resulting values for the initial pressures of ideal gases in the system P_{1n} and P_{2n} make it possible to rewrite ratios (16) and (17) in the following way:

$$G_{1n} = n_1(G_1^0 + RTlnRT\frac{n_1}{V_1}) \,, \tag{25}$$

$$G_{2n} = n_2(G_2^0 + RTlnRT\frac{n_2}{V_2}) \,. \tag{26}$$

Equations (21) and (22) characterize the system in question after the mixing process. In this case, taking into account the fact that both gases will be in the same volume $V = 1$, the following statement will be fair for them:

$$P_{1k} = n_1RT \,, \tag{27}$$

$$P_{2k} = n_2RT \,. \tag{28}$$

The resulting final values of ideal gas pressures in the system P_{1k} and P_{2k} make it possible to write the ratios (18) and (19) as follows:

$$G_{1k} = n_1(G_1^0 + RTlnn_1RT) \,, \tag{29}$$

$$G_{2k} = n_2(G_2^0 + RTlnn_2RT) \,. \tag{30}$$

This allows to integrate the expression (14), which determines the change in free diffusion energy when two different ideal gases are mixed, from the initial to the final value of that energy. Thus, the change in the value of the Gibbs free energy of diffusion ΔG_d will be determined by the following:

$$\Delta G_d = G_{1k} + G_{2k} - G_{1n} - G_{2n} \,. \tag{31}$$

After substituting previously obtained ratios for G_{1n}, G_{2n}, G_{1k} and G_{2k}, and making elementary algebraic transformations, we can get the value of characteristic change of Gibbs free energy ΔG_d caused by the diffusion process in the system under consideration, namely:

$$\Delta G_d = n_1RTlnV_1 + n_2RTlnV_2 \,. \tag{32}$$

We need to note that in this equation both V_1 and V_2 are less than one, which automatically leads to $\Delta G_d < 0$, in other words, it indicates the spontaneity of the diffusion process, which is observed in practice. However, the diffusion equalization of chemical potentials has no effect on the energy of particle interaction, as the ideality of the system in question (a mixture of ideal gases, ideal solid or liquid solutions) does not get violated according to the definition of such systems above, which means that the energy of their chemical interaction is invariable.

Thus, we can argue that the original state of the system in question is characterized by some integral amount of free energy, including, among other things, free energy of diffusion G_d. The latter, as is obvious from the previous text, does not refer to the individual components of the system under consideration, but to it as a whole. This circumstance allows us to write the following equation:

$$G_n = G_{1n} + G_{2n} + n_1 RTlnV_1 + n_2 RTlnV_2 . \tag{33}$$

When we include the values of G_{1n} and G_{2n} and carry out elementary algebraic transformations, we get:

$$G_n = n_1 G_1^0 + n_2 G_2^0 + n_1 RTlnn_1 RT + n_2 RTlnn_2 RT . \tag{34}$$

At the same time, we can argue that the final state of the system in question is characterized by the following amount of free energy G_d (free diffusion energy in this case is zero):

$$G_k = G_{1k} + G_{2k} . \tag{35}$$

When we substitute the values of G_{1n} and G_{2n}, and perform elementary transformations accordingly, we get:

$$G_k = n_1 (G_1^0 + RTlnn_1 RT\ ) + n_2 (G_2^0 + RTlnn_2 RT) . \tag{36}$$

So, for the change in the Gibbs free energy $\Delta G_{1,2}$ when mixing two different ideal gases, we get:

$$\Delta G_{1,2} = G_{1k} + G_{2k} - G_{1n} - G_{2n} . \tag{37}$$

Substituting the values G_{1k}, G_{2k}, G_{1n} and G_{2n}, as well as making elementary algebraic transformations, taking into account the comments made by us earlier, allows us to finally write down:

$$\Delta G_{1,2} = n_1 RTlnV_1 + n_2 RTlnV_2 . \tag{38}$$

Concluding this subsection of the article, we need to emphasize that the latest formula describes the change in the Gibbs energy when two not necessarily identical portions of different ideal gases are mixed. This also takes into account the change of free energy of diffusion, inherent to the system under consideration as a single whole.

3.3. Discussion of the results and their verification

The calculations carried out in the two previous subsections of this work allow us to draw a completely unambiguous conclusion that when two portions of ideal gases are mixed, there is no change in their molar characteristics. In turn, taking into account the free diffusion energy, inherent to the system in question with two different ideal gases as a single whole, leads to a decrease in this type of energy. In other words, the amount of change in the energy characteristics of the object in question, such as, for example, low-alloy carbon steel, depends on their starting point of reference, i.e. the presence (or lack of) free diffusion energy, inextricably linked to the system being considered as a single whole, and not its individual parts.

Now we will demonstrate that the results are well consistent, at least, with some features of corrosive behavior of alloys. For this purpose, we will consider the process of electrochemical interaction of amalgams of different metals with the environment. In this case, according to the ideas developed in particular by H. Kaesche [15, pp. 36–49], the equilibrium potential of the liquid alloy is determined by the following ratios:

$$E = E^0_{Hg/Hg_2^{2+}} + \frac{RT}{2F} ln \frac{C_{Hg_2^{2+}}}{1-\gamma_{Me}} = E^0_{Me/Me^{z+}} + \frac{RT}{zF} ln \frac{C_{Me^{z+}}}{\gamma_{Me}} , \tag{39}$$

where: E is the equilibrium electrode potential of the amalgam; $E^0_{Hg/Hg_2^{2+}}$ is the standard value of the mercury electrode's potential; $E^0_{Me/Me^{z+}}$ is the standard value of the potential of the metal (not mercury) electrode, which is part of the amalgam in question; $C_{Hg_2^{2+}}$ is the concentration of mercury ions in the electrolyte solution; $C_{Me^{z+}}$ is the concentration of metal (not mercury) ions in the electrolyte solution; γ_{Me} is molar fraction of metal in the amalgam.

It is obvious that for the liquid binary alloy (metal amalgam) in question, the ratio between the molar fraction of mercury γ_{Hg} and metal γ_{Me} in amalgam can be written as:

$$\gamma_{Hg} = 1 - \gamma_{Me} \tag{40}$$

A simple analysis of the equation (39) shows that the equilibrium potential of the amalgamated electrode is achieved at a double equilibrium [15, p. 49]. In this case, with the set of molar and atomic fractions γ_{Hg} and γ_{Me} in the amalgam, in the solution there is a fully defined ratio of activities or concentrations of mercury ions and ions of the metal dissolved in it a_{Hg} / a_{Me}. We can find similar equations in the works of other authors, for example, L.I. Antropov, where he is considering the behavior of amalgam electrodes. Thus, we should note that the change in the energy state of the system associated with the formation of the alloy (ideal system), which is represented by ratios (1) and (2), in no way affects its equilibrium potential and the speed of its anode dissolution. In general, this situation seems quite logical. This is due to the fact that the thermodynamics of the transition of ions across the boundary of the phase section of binary alloy–electrolyte, which is actually responsible for establishing a state of equilibrium in the system in question, is determined solely by the strength (energy) of the connections of ions under consideration in these systems, naturally, with equal energy of their solvation (hydration). We should note that under ideal conditions, the process of alloy formation has no effect on the process of transition of ions, i.e. a kind of "diffusion component of potential" presented by equations (1) and (2) of course should be absent. However, this is indirectly confirmed by I.K. Marshakov himself. Indeed, he does not use the conclusions of one of the sections of his monograph [13, pp. 89–91] dedicated to the thermodynamic preconditions of alloy formation in any way. This fact indicates, at least, the lack of verification process. On the other hand, the formation of real alloys, for example, high-alloy steels as opposed to ideal alloys, is already associated with changes in the chemical energy. This becomes especially noticeable in the case of the formation of new chemical bonds, for example, in the formation of intermetallic compounds, which is usually accompanied by the release or absorption of heat in the process under consideration [16, p. 67]. This fact unequivocally will affect the strength of chemical bonds in a solid solution (alloy), which is noted, for example, in the paper [14], and, consequently, will change the equilibrium potential of the real binary alloy, which, in its turn, significantly affects the kinetics of electrochemical corrosion and, consequently, the rate of its anode dissolution. A more detailed analysis of the problem under consideration can be conducted based on the Terrace Ledge Kink model, which is used in practice during consideration of electrochemical dissolution of metals, which, in particular, was successfully demonstrated by K. Fetter in his classic monograph [17, pp. 313–354]. However, in our fairly simple case of anode dissolution of binary alloys, it is quite possible to limit ourselves to the illustration of this process, given in the book by N.D. Tomasov and G.P. Chernova.

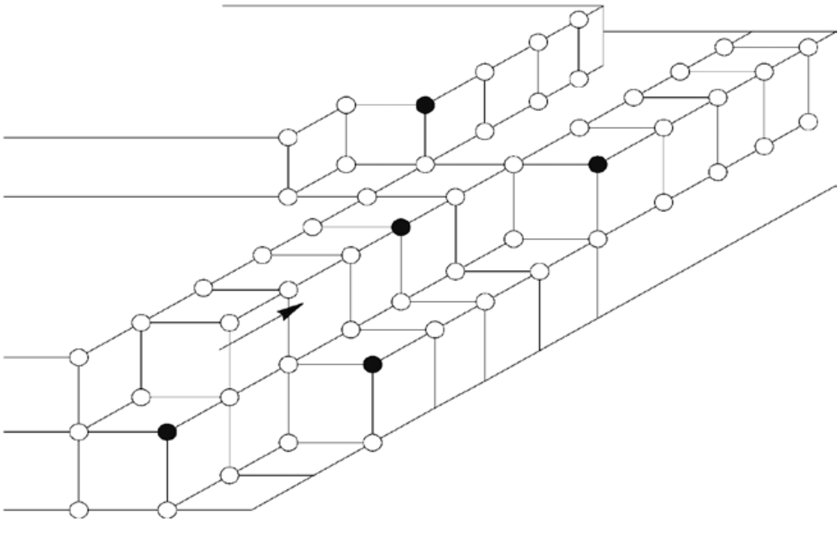

Figure 1. Scheme of anode dissolution of cubic crystal lattice of binary alloy of the solid solution type. Dark dots are the atoms of the doping component.

In this case, within the framework of the scheme proposed by Kossel and Stranski, dissolution of metals that make up, for example, the cubic crystal lattice of the binary alloy (the system forms a substitutional solid solution) is carried out from different energy points of its crystal lattice, at the same time [16, p. 69] "the lesser the number of the adjacent atoms with which the atom is associated, the bigger it is energy opportunities, and therefore the more negative its electrochemical potential and the more likely its ionization and transition into the solution." This picture becomes even more prominent if we have, for example, a binary substitutional solution illustrated in Fig. 1, where the dark dots represent the atoms of the doping component. In this case, during dissolution according to the scheme presented by the arrow in the mentioned figure, more resistant atoms (the doping component) will gradually appear "in more active places", namely in the corners of the edges of the crystal lattice and thus slow down the overall rate of anode dissolution of the alloy. On the other hand, if we assume that the energy characteristics of all atoms are identical and in the formation of the ideal solid solution remain unchanged, which, however, directly follows from its definition, then the only changing parameter, in addition to the existing concentration changes in the alloy, is the energy of solvation (hydration) of the atoms of the system in question. Thus, the kinetic analysis of the process of anode dissolution of low-doped binary alloys in the approximation of ideal solid solutions clearly demonstrates the independence of its electrochemical behavior (the rate of anode dissolution) from the process of its formation from the pure original components. However, taking into account the experimental data on the reduction of free energy in the formation of non-ideal alloys such as solid solutions [16, p. 67], the value of which is estimated to be about a thousand calories (4187 joules) per gram-atom, "which corresponds to a change in the electrochemical potential of the components in a positive direction by about 20 mV." We should note on our own that it is fair for divalent metals, for monovalent metals this value will already equal approximately 40 mV. At the same time, it is known that "The decrease in free energy during corrosion reactions for technical (base) metals can amount to tens and hundreds of thousands of calories per gram-atom, i.e. it will correspond to the EMF corrosion process of about 200–2000 mV" [16, p. 67], which corresponds to approximately the interval from 41870–418700 joules. It would seem that the contribution of "ideality" in the formation of an alloy (approximately 20–40 mV) in its corrosive behavior, caused by the alloy-electrolyte relationship (200–2000 mV) is extremely small, i.e. ranges from one to twenty percent. However, this impression is deeply misguided. Very often, especially in atmospheric and soil corrosion, corrosive vapors are formed, EMF of which can be compared with the values under consideration [18]. Figure 2 illustrates this statement.

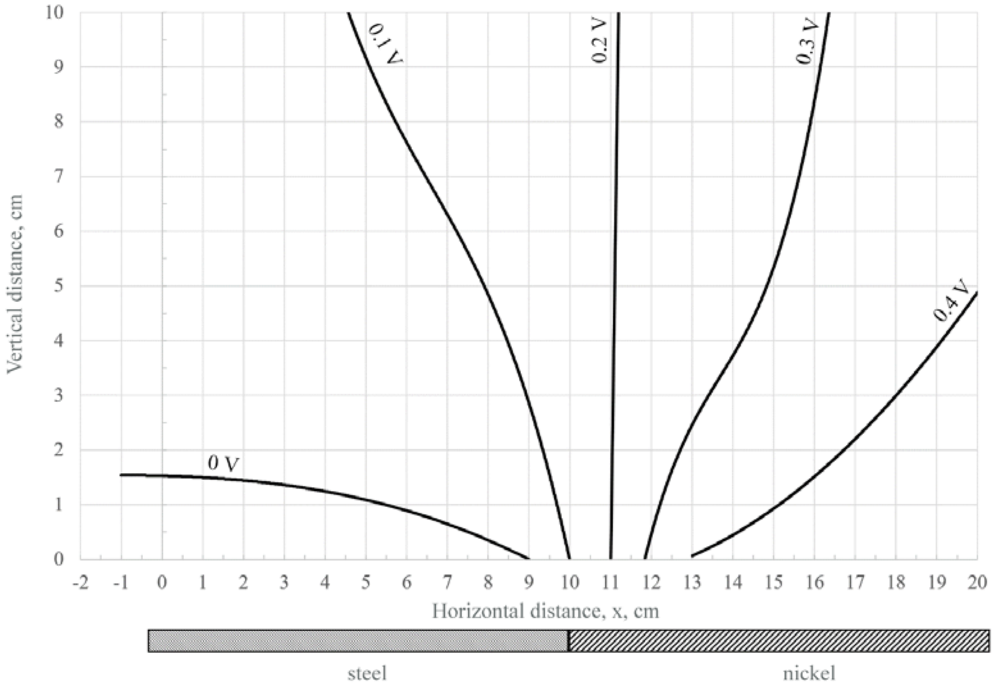

Figure 2. Potential field over a flat short-circuited element with a steel anode and a nickel cathode in tap water. The potential is related to the potential of corrosion of the anode.

It is appropriate to compare the given data on the "inediality" of a solid solution with the change in the free energy, which is observed in the formation of ideal solutions. In this case, as we have established earlier, the formula (38) "works", which for the case under consideration is more convenient to present in the following form [13, p. 30–31].

$$\Delta G_{1,2} = N_1 RTlnN_1 + N_2 RTlnN_2 \tag{41}$$

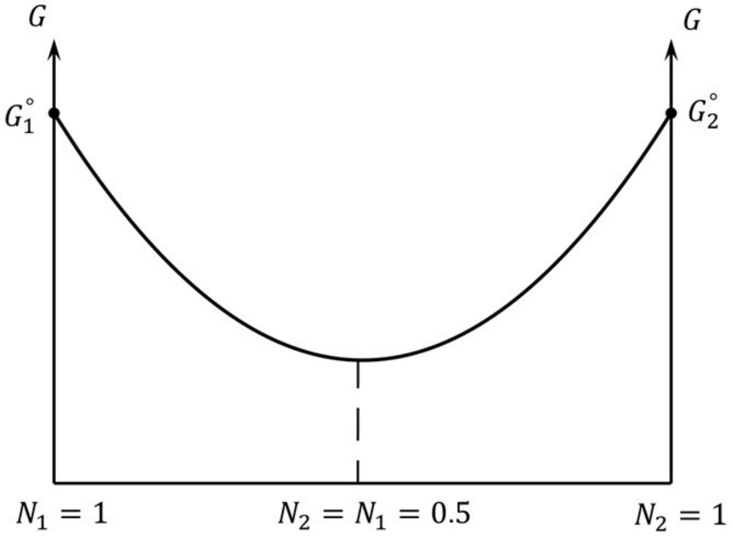

Figure 3. Dependence of the Gibbs free energy (diffusion component) of the ideal binary alloy from its chemical composition in the ideal solid solution approximation.

Where N_1 and N_2 are molar fractions of respectively the first and second components of the alloy, and $\Delta G_{1,2}$, as before, refers to one mole of the solution (alloy); Accordingly, $\Delta G_1 = N_1 RTlnN_1$ and $\Delta G_2 = N_2 RTlnN_2$.

A respective graph of change of the "ideal" Gibbs free energy (diffusion component) is presented on the Figure 3 and represents some curve with a minimum [13, p. 22].

Table 1. Changes in Gibbs free energy (diffusion component) in the formation of the ideal binary alloy (solid solution) as a function of changing the molar fractions of the alloy components.

Indicators	1	2	3	4	5
N_1	0.5	0.1	0.01	0.001	0.0001
N_2	0.5	0.9	0.99	0.999	0.9999
$\Delta G_{1.}$	- 844.20	- 561.01	-112.18	- 16.83	-2.24
ΔG_2	- 844.20	- 231.08	- 24.12	- 2.43	- 0.24
$\Delta G_{1.2}$	- 1688.40	- 792.09	- 136.30	-19.26	-2.48

Values of the $\Delta G_{1,2}$ are listed in joules per mole of the alloy, and the partial molar values $\Delta G_1 = N_1 RTlnN_1$ and $\Delta G_2 = N_2 RTlnN_2$, listed in joules, are normalized by their molar fractions in the alloy.

However, due to the fact that this dependence shows only trends of changes in $\Delta G_{1,2}$, and therefore does not allow to determine the specific values of the change of free energy, for the subsequent comparative analysis we will have to present them in a table form. We will do this for five different cases of the ratio of the molar fractions of the initial components in the alloy, numbered from 1 to 5 (during the calculations, the conventional temperature of the solution formation was chosen equal to 20 ℃).

The simplest analysis, of the both graphical dependence and table data, shows that firstly the change in molar free energy formation of the ideal alloy even at its maximum absolute value (equal original alloy components, column 1) is relatively small compared to the experimentally observed magnitudes of the formation of real alloys and in this case the ratio is approximately equal to 0.04 (1688.40/41868 ≈ 0.04), and secondly, when the molar fraction of one of the components (in our case, N_1) begins to decrease even more markedly in the absolute value of this indicator and, for example, for the column 5 it is already a small fraction, namely 0.00006 (2.48/41868 ≈ 0.00006). We should note that for the calculations carried out in the latter case, we used the minimum possible value of the "chemical" component of the free energy, equal, as we have established earlier, to 41870 joules. The data obtained are undoubtedly an additional and very strong argument in favor of the practical absence of the effect of the process of formation of the ideal binary alloy on the nature of its possible further anode dissolution.

We should note that in the modern construction industry and the industries that serve it, a lot of attention is paid to the actual problem of materials science [19–22], as well as the issues of preserving the strength characteristics of the materials used. A logical continuation of this trend is the presented work on the study of corrosive behavior of low-alloy steels. This material-scientific problem is also in the trend of modern science, as evidenced by the numerous publications on this topic [23–30], which argues for the relevance of the research presented in this paper. This article is, to some extent, a continuation and development of previous publications [14, 31–36] devoted to the consideration of the process of mixing ideal gases and in no way contradicts them. At the same time, it aims to address the very specific and extremely important problem of increasing the corrosion resistance of carbon and low-alloy steels, which play a very important role in almost every area of human activity, especially in the field of construction and architecture. This research, focused primarily on the study of ideal binary alloys that are models of real carbon and low-alloy steels, allows us to draw conclusions presented below.

4. Conclusions

1. The equilibrium potential of the ideal binary alloy in the electrolyte is by no means dependent on the process of its formation from the pure raw components, but is determined solely by the ratio of energy characteristics of the ions of metals located actually in the alloy, as well as the energy characteristics of the same ions in the electrolyte solution that comes into contact with the alloy.

2. The presence of the Gibbs free energy, which characterizes the diffusion behavior of two generally different portions of different components of the ideal binary alloy and, accordingly, the process of its formation, in no way affects the speed of its anode dissolution.

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Contacts:

Vladimir Kiselev, kis_vg@mail.ru
Aleksandr Kalyutik, AA_Kalyutik@spbstu.ru