Physical Chemistry

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1960

SovietRxiv

Abstract

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On the Question of the Influence of Temperature on the Rate of Corrosion of Metals in Acidic Media

(Presented by Academician V. I. Spitsyn, 10 III 1960)

The dependence of the reaction rate on temperature, established as early as 1889 by Arrhenius, has a general character and, with a fairly high degree of accuracy, is applicable to heterogeneous reactions, in particular to corrosion processes. For these latter cases the indicated dependence can be expressed by the equation

$$K = A \exp\left(-\frac{E_{\text{eff}}}{RT}\right), \tag{1}$$

where A is a constant and E_{eff} is the effective activation energy. As a result of taking logarithms of expression (1), the equation of a straight line is obtained,

$$\lg K = \lg A - \frac{E_{\text{eff}}}{2.303RT}, \tag{2}$$

on the basis of which one can calculate the values of K for intermediate temperatures without studying them experimentally, and also determine the values of the apparent activation energy.

Many investigators ($^{1-3}$) believe that, for acidic media and comparatively active metals, the Arrhenius dependence is obeyed with a sufficient degree of accuracy. In works (^{4,5}) and others, a linear dependence of current density on $1/T$ has been established, having a form identical with equation (1). At $\Delta\varphi = \text{const}$, this dependence is linear over a considerable potential interval. However, data may be found in the literature indicating that the above dependence is not always obeyed.

Deviations from the Arrhenius equation are especially frequent for cases of corrosion of metals proceeding with oxygen depolarization in open systems, where the decrease in the corrosion rate with increasing temperature is associated with a decrease in the solubility of oxygen; dependence (2) in coordinates $\lg K$—$1/T$ in these cases is often expressed by a curve with a maximum (^{5}). The rectilinearity of the dependence $\lg K = f(1/T)$ is not always observed in cases of gas

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

corrosion either, if, in particular, a change in the crystalline structure of the metal takes place (for example, the transition α-Fe —γ-Fe).

Gutman and Simons (^{6}) believe that deviations from the linear dependence $\lg K = f(1/T)$ are associated either with the fact that the constants A and E_{eff} in equation (1) change substantially with temperature, or with the fact that the simultaneous occurrence of a number of reactions is observed.

Investigating the influence of temperature on the corrosion rate of certain metals (steels Fe, Ni, Zn, Al, Cu, Cd, Sn, Pb) in acidic media ($1N$ solutions of HCl and H_2SO_4), we, along with the rectilinear form of the dependence $\lg K = f(1/T)$, encountered a number of deviations from it. Iron, steel, nickel, tin, cadmium, and aluminum (the latter only in $1N$ sulfuric acid) follow the Arrhenius equation more or less rigorously both in sulfuric and hydrochloric acid solutions (Fig. 1).

But in studying the dependence of the corrosion rate of aluminum on temperature in a $1N$ solution of hydrochloric acid, we observed a sharp increase in the corrosion rate with temperature, considerably exceeding the values following from equation (2) (Fig. 2). Such a deviation becomes noticeable at temperatures exceeding 40°C. Naturally, at the same time the values of E_{eff} and the temperature coefficients of corrosion increase strongly. Such behavior of aluminum in hydrochloric-acid solutions may be explained by the fact that, under the influence of elevated temperature and a significant concentration of aggressive chloride ions, the oxide film on aluminum—usually stable in acids—is destroyed, in particular its pseudomorphic layer. It should also be taken into account that under these conditions aluminum exhibits the influence of a negative difference effect, first established by N. D. Tomashov and T. V. Matveeva (^{7}).

Fig. 1. Dependence of the common logarithm of the corrosion rate of metals on reciprocal absolute temperature.
1—Armco iron, 2—nickel, 3—tin, 4—cadmium, 5—aluminum; a—in $1N$ H_2SO_4, b —in $1N$ HCl.

Fig. 2. Dependence of the common logarithm of the corrosion rate of aluminum on reciprocal absolute temperature in $1N$ HCl.

A directly opposite phenomenon was observed in studying the corrosion of technical aluminum (Al-2) in concentrated ($35N$) sulfuric acid. Here, as in the preceding case, up to a temperature of 50-60°C the corrosion rate increases in accordance with the Arrhenius equation, but at higher temperatures it decreases markedly (Fig. 3). On the curve in the coordinates $\lg K$—$1/T$, a maximum is observed at about 70°C. In the interval 60-80°C, the values of E_{eff} proved to be negative. The described phenomenon can be quite satisfactorily interpreted as

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

the transition of aluminum under these conditions into the passive state. Evidently, the oxidizing action of sulfuric acid increases substantially both with an increase in its concentration and with a rise in temperature. As a result, the film covering the bottoms of the pores becomes only slightly permeable to Al^{3+} ions; the pore dimensions decrease, which leads to passivation of aluminum and to a decrease in the corrosion rate.

An almost analogous picture occurs in studying the influence of temperature on the corrosion rate of copper in $1N$ solutions of these same acids (Fig. 3), which may be explained by the decrease in the solubility of oxygen in an open system with rising temperature.

We also observed cases of a slight deviation of the straight line $\lg K = f(1/T)$ at elevated temperatures toward the axis of reciprocal absolute temperatures (zinc, lead in both acids) (Fig. 4). Apparently, the reason for this phenomenon lies in the fact that an increase in temperature leads to an increase in the rate of both chemical and diffusion processes, but the rate of the former outstrips the rate of the latter ([8]). As a result, at sufficiently high-

At high temperatures the role of the diffusion factor acquires great importance, and sometimes a controlling one. This is especially clearly manifested for lead, which is also connected with the shielding of its surface by phase salt films.

The results of our investigations presented above allow us to conclude that the corrosion rate of metals in acid media changes with temperature in accordance with the dependence established by Arrhenius only in the absence of complicating factors. If, however, with an increase in temperature there have been changes in the structure of the metal, the existing oxide film has been destroyed, or a passive state of the metal has set in, then the corrosion rate may change with temperature in such a way that it ceases to obey the Arrhenius equation, and dependence (2) is replaced–

Fig. 3. Dependence of the common logarithm of the corrosion rate of metals on reciprocal absolute temperature.
1*a*–copper in $1\,N$ H_2SO_4; 1*b*–copper in $1\,N$ HCl; 2–aluminum in $35\,N$ H_2SO_4

Fig. 4. Dependence of the common logarithm of the corrosion rate of metals on reciprocal absolute temperature.
1–zinc, 2–lead; *a*–$1\,N$ H_2SO_4; *b*–$1\,N$ HCl

by a more complex one. Deviations from dependence (2) may be of either sign. There is also no doubt that at sufficiently high temperatures cases of a certain deviation from a straight line on the plot $\lg K—1/T$ toward the axis of reciprocal temperatures are caused by a more retarded increase in the rate of diffusion processes as compared with the increase in the rate of chemical processes.

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Received
9 III 1960

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