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## Abstract

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# THE EFFECT OF ADSORBED HALIDES ON THE ELECTRON WORK FUNCTION OF IRON

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In the work of our laboratory [1–3] on the influence of adsorbed oxygen on the electron work function of iron, nickel, and platinum, it was shown that not only the magnitude but also the sign of the contact potential difference is determined by the conditions of interaction of the gas with the metal. Thus, upon adsorption of one and the same amount of oxygen on iron and nickel, the electron work function increases or decreases depending on the temperature of interaction of the gas with the metal. In the case of iron, reversal of the sign of the surface charge also occurs when the amount of adsorbed oxygen is varied. A similar influence of chemisorbed oxygen on the surface charge has recently also been observed by other authors [4].

In connection with the data presented above, it was of interest to investigate the effect of other electronegative gases adsorbed on metals–for example, halides–on the electron work function. The literature on the influence of halide adsorption on the electron work function is extremely limited. The work of Ule and Ripl [5] showed that iodine and bromine adsorbed on the surface of gold, and iodine on silver, cause an increase in the electron work function. Iodine also increases the electron work function of zirconium and titanium [6]. The change in work function in the case of Ag, Au, and Zr was 0.2–0.4 V, while for Ti $\Delta\varphi$ reached 0.9 V. A different dependence was observed upon adsorption of halides on alkali-group metals, where adsorption leads to a decrease in the electron work function [7].

In the present work we investigated the effect of chlorine and iodine adsorbed on iron under various conditions on the electron work function. The contact potential difference was measured by the vibrating-capacitor method [8], in an apparatus in which the molybdenum reference electrode was sealed into glass, analogous to that described in the work of R. Kh. Burstein and L. A. Larina [9]. The electrode under study was a plate measuring 20 × 20 × 0.2 mm made of spectrally pure iron from the firm "Hilger."

Chlorine was obtained by thermal decomposition of gold chloride [10]. After conditioning in vacuum, gold chloride or iodine was heated, and the evolved

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

vapors of chlorine or iodine were condensed in a side arm immersed in liquid nitrogen. To dose chlorine or iodine, a definite vapor pressure of the halide was maintained in the apparatus; this was achieved by immersing the side arm with the condensate in various cooling mixtures. In this way, ampoules with different pressures of chlorine or iodine were obtained. As cooling mixtures for dosing chlorine, the following were used: solid isopentane ($t_{\mathrm{m}} = -142°$), solid ethyl alcohol ($t_{\mathrm{m}} = -106°$), and a mixture of solid carbon dioxide with acetone ($t = -78°$), which corresponded to chlorine vapor pressures in the ampoule of $4 \cdot 10^{-2}$ mm, 5 mm, and 63 mm Hg [11]. After breaking the ampoule, the chlorine vapor pressure in the system corresponded to $4 \cdot 10^{-4}$ mm, $5 \cdot 10^{-2}$ mm, and $6.3 \cdot 10^{-1}$ mm Hg. The iodine vapor pressure in the system in our experiments corresponded···

was 0.01 mm and 0.07 mm Hg. To check the accuracy of the dosing of the halides, analytical determinations of the chlorine and iodine content in the ampoules were carried out by the iodometric method. The analytical data agree satisfactorily with the amount of halides determined from the equilibrium values of the vapor pressure.

The preliminary treatment of the iron electrode consisted in repeated reduction with hydrogen at a temperature of 400° and subsequent prolonged degassing to a pressure of $2 \cdot 10^{-6}$ mm Hg while heating by high-frequency currents to 700°. The cell was then placed in a copper-mesh shield and, in order to remove induced effects, was heated to 200° by direct current.

Fig. 1. Effect of the heating temperature of iron with chemisorbed chlorine in vacuum on the contact potential difference:
$I$ –chemisorption at 20°, $p = 5 \cdot 10^{-4}$ mm Hg; $II$ –the same at $p = 5 \cdot 10^{-2}$ mm; $III$ –the same at $p = 6 \cdot 10^{-1}$ mm

Fig. 2. Change in the contact potential difference as a function of the temperature of interaction of chlorine with iron at various chlorine pressures in the gas phase:
$I$ –$p = 5 \cdot 10^{-4}$ mm Hg; $II$ –$p = 5 \cdot 10^{-2}$ mm; $III$ –$p = 6 \cdot 10^{-1}$ mm

After the apparatus had been cooled to room temperature, the contact potential difference between the iron and the reference electrode was measured. By breaking the ampoule, chlorine or iodine vapors were introduced into the system. The iron electrode was kept at room temperature (20°) in halide vapors for 15-17 h, and the contact potential difference was again measured.

Figure 3

Figure 3: Figure 3

To determine the dependence of the electron work function on the conditions of interaction of chlorine with iron, the contact potential differences between pure iron and iron that had absorbed chlorine were determined both at different halide pressures in the system and at one and the same pressure but at different temperatures (20-300°). Independently of the interaction conditions, all measurements of the contact potential difference were made at 20°. The results obtained are presented in Figs. 1 and 2. The given values of the contact potential difference are mean values from a series of experiments. The greatest deviation from the mean value was 25%.

The change in the electron work function upon adsorption of chlorine on iron is caused by irreversible chemisorption. This is evident from the fact that, upon degassing the apparatus after chlorine adsorption, the work function does not change. The latter also indicates that chlorine has no effect on the reference electrode. In studying the effect of chlorine adsorbed at 20° on the electron work function, it follows that changing the pressure from $4 \cdot 10^{-4}$ to $6.3 \cdot 10^{-1}$ mm Hg leads to a change in the contact potential difference from 0.1 to 0.27 V. Heating iron with chemisorbed chlorine to 100° in the absence of chlorine in the gas phase (the chlorine was frozen out with liquid nitrogen) leads to an additional increase in the work function, reaching, as is seen from curve $III$, 0.85 V. After the electrode temperature is raised to 200-300°, a decrease in the electron work function is observed in comparison with the preceding value. After heating the electrode at 300°

the electron work function becomes smaller than that from reduced iron. As is seen from curves *II* and *III*, this decrease reaches 0.1 V. In the presence of chlorine in the gas phase (Fig. 2), an analogous temperature dependence is observed. The difference consists only in the fact that the maximum value of the contact potential difference, 1.3 V, in this case corresponds to heating at 200°. After heating at 300° there is some decrease in the electron work function, but it is nevertheless higher than that from the reduced metal. The dependences of the contact potential difference on the vapor pressure of chlorine in the gas phase at various absorption temperatures are given in Fig. 3. As is seen from Fig. 3, over the entire temperature interval investigated (20-300°), increasing the chlorine pressure in the system causes an increase in the electron work function.

Fig. 3. Effect of chlorine pressure on the contact potential difference: $a$ –20°, $b$ –100°, $v$ –200°, $g$ –300°.

The increase in the electron work function on iron upon adsorption of chlorine on it at room temperature may be explained by the formation, on its surface, of dipoles oriented with the negative sign outward. The further increase in the electron work function observed on iron with increasing temperature of

Figure 4

Figure 4: Figure 4

interaction with chlorine cannot be explained solely by a change in the amount of adsorbed halide. This conclusion is based on the fact that an analogous increase occurs after heating iron with chemisorbed chlorine in vacuum, i.e., under conditions where additional adsorption is impossible. To explain the phenomenon described here, it must be assumed that increasing the temperature leads to a change in the nature of the bond between chlorine and the surface iron atoms.

The decrease, in comparison with its maximum value, of the magnitude of the contact potential difference at temperatures above 100° in vacuum and 200° in the presence of chlorine in the gas phase is associated with the occurrence of two processes. First, removal of ferric chlorides from the electrode surface takes place, as may be judged by the appearance in some cases of a slight brown deposit on the cell walls. According to literature data ([12]), the vapor pressure not only of ferric chloride but also of ferrous chloride at temperatures of 200° and above is already appreciable. Second, penetration of halide atoms under the upper layer of iron atoms or the emergence of iron atoms onto the surface of the chloride is possible. This follows from the fact that the electron work function from iron that has absorbed a certain amount of chlorine, after heating to 300°, becomes smaller than that from the reduced and degassed electrode. In the presence of chlorine in the gas phase, in the temperature interval 100-200°, additional absorption of halide occurs, which leads to a change in the electron work function reaching 1.3 V.

Fig. 4. Change in the contact potential difference as a function of the heating temperature of iron with chemisorbed iodine. *I* —heating in vacuum after chemisorption of iodine at $p = 1 \cdot 10^{-2}$ mm Hg and 20°; *II* —the same at $p = 7 \cdot 10^{-2}$ mm and 20°; *III* —heating at an iodine pressure in the gas phase of $p = 1 \cdot 10^{-2}$ mm Hg; *IV* —the same at $p = 7 \cdot 10^{-2}$ mm.

To determine the influence of adsorbed iodine on the electron work function from iron, a series of experiments was carried out at pressures of 0.01 and 0.07 mm Hg. The results obtained are presented in Fig. 4.

In contrast to the results obtained with chlorine, the maximum increase in the electron work function is observed for iodine chemisorbed on iron at 20°. The contact potential difference at a pressure of 0.07 mm Hg reaches 0.5 V. Removal of iodine from the gas phase after chemisorption on the iron surface does not lead to a change in the contact potential difference, which indicates the irreversibility of the process. Raising the temperature of the interaction of iodine with iron leads to a gradual decrease in the electron work function compared with the value obtained at 20°. After heating at 300°, the electron work function becomes lower than the work function of pure iron by 0.1-0.15

V. From the results obtained it follows that the value of the contact potential difference increases with increasing iodine pressure, which may be connected with an increase in the rate of chemisorption of iodine as the pressure is raised.

On the basis of these data it may be assumed that absorption of iodine atoms at room temperature is accompanied by transfer of an electron from the metal to the halide, leading to the appearance of a negative charge on the surface. The subsequent decrease in the electron work function as the temperature of interaction is raised is apparently caused by evaporation of the ferric iodide formed ([13]), as evidenced by the yellow-brown deposit on the walls of the cell, in which iron ions were detected.

The decrease in the electron work function of iron with chemisorbed iodine after heating at 300°, compared with pure iron, can be explained in the same way as the analogous phenomenon with chlorine described above.

It follows from the data obtained that, in the chemisorption of halides on iron, as in the chemisorption of oxygen, an increase or decrease in the electron work function is observed depending on the conditions of interaction.

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