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Abstract

Full Text

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE INFLUENCE OF ABSORBED FLUORINE ON THE ELECTRON WORK FUNCTION OF IRON

(Presented by Academician A. N. Frumkin, October 9, 1963)

In previous works from our laboratory it was shown ^(1,2) that oxygen, chlorine, and iodine, depending on the conditions of interaction with iron (temperature, pressure), can increase or decrease the electron work function. Of the gases previously investigated, the greatest decrease in the electron work function was observed during chemisorption of oxygen. In connection with this, it was of interest to investigate the influence of chemisorbed fluorine, the most electronegative gas, on the electron work function of iron.

As the objects of investigation we used a plate, 0.2 mm thick, of spectrally pure iron (Hilger) and fluorine containing 99% F_2 (the 1% of impurities consisted mainly of noble gases). The fluorine was additionally purified from HF by passing it through a trap immersed in liquid nitrogen. The iron was repeatedly reduced with hydrogen at 450–480° and then degassed by heating with high-frequency currents to a temperature of 700–800°. The contact potential difference was measured by the vibrating-capacitor method with a molybdenum reference electrode sealed in glass ⁽³⁾. Fluorine was introduced into the system by breaking, with the aid of an electromagnetic device, glass ampoules filled with fluorine. The volume of the ampoules and the fluorine pressure in them were chosen so as to establish a definite pressure in the system. Instead of stopcocks, the system used ball-shaped membranes in combination with constrictions for sealing off. The membranes were broken with the aid of electromagnets.

In order to judge the changes in the contact potential difference during chemisorption of fluorine as a function of the temperature of its interaction with iron, the following measurements were carried out.

After determining the contact potential difference between the reduced and degassed iron electrode and the reference electrode, fluorine was introduced into the apparatus; its pressure in the series of experiments described here was $6 \cdot 10^{-2}$ mm Hg, and the contact potential difference was measured again. The fluorine was then removed from the system by adsorption on activated charcoal at the temperature of liquid nitrogen, followed by evacuation to a pressure of 10^{-7} mm Hg. After measurement of the contact potential difference, the iron

Fig. 1

Figure 1: Fig. 1

electrode that had absorbed fluorine at 20° was successively heated in vacuum at 100, 200, and 300° for 1.5 hours, and the contact potential difference was again measured at each of the indicated temperatures, as well as after cooling to room temperature.

Figure 1 shows the change in the surface potential of iron after its interaction with fluorine at 20° and subsequent heating in vacuum over the temperature interval 20-300°. The contact potential difference in the case of curve 1 was measured during heating, and in the case of curve 2 after cooling to room temperature.

It follows from the results obtained that, upon adsorption of fluorine, the value of the surface potential shifts in the positive direction, which

indicates a decrease in the electron work function. The greatest decrease in the electron work function is observed when iron interacts with fluorine at room temperature and amounts to 0.6-0.7 V. In the temperature interval 100-300° the contact potential difference had an almost constant value equal to 0.4 V.

Thus, the absorption of fluorine, which has the highest electronegativity value, leads to a considerable decrease in the electron work function.

A comparison of these data with those obtained earlier ⁽⁴⁾ in studying the interaction of iron with oxygen leads to the conclusion that at room temperature chemisorption of fluorine causes a greater decrease in the work function than chemisorption of oxygen.

According to generally accepted ideas, adsorption on metals of oxygen and halogens, which have a high electron affinity, should be accompanied by transfer of an electron from the metal to the adsorbate. This in turn should lead to the appearance of a negative charge on the surface and to an increase in the electron work function. However, as follows from Fig. 2 (curve 1), the electron work function of iron after adsorption of oxygen, fluorine, chlorine, and iodine ^(2,4) is the smaller, the higher the electronegativity of the adsorbate ⁽⁵⁾. At the same time, in Fig. 2 (curve 2) these values of the contact potential difference are compared with the sizes of the ionic radii of the corresponding substances. From the curve shown it follows that the value of the positive charge on the surface increases as the radius of the adsorbate ion decreases.

Fig. 1. Change in the c.p.d. as a function of the temperature of interaction of fluorine with iron at a pressure of $6 \cdot 10^{-2}$ mm Hg. **1** —on heating, **2** —on cooling to 20°.

Fig. 2. Dependence of the change in the electron work function of iron during chemisorption of oxygen and halogens on the electronegativity of the adsorbate

Fig. 2

Figure 2: Fig. 2

and the radius of its ion. **1** —on the electronegativity value (χ), **2** —on the value of the ionic radius (r).

According to the ideas expressed by us earlier, and recently accepted by a number of other investigators⁽⁶⁻⁸⁾, the decrease in the electron work function upon adsorption of electronegative substances apparently results from the “creeping” of the adsorbate under the upper layer of metal atoms, or from the emergence of the latter onto the surface of the adsorbed layer. In the first case, the size of the adsorbate ion plays a decisive role in its penetration between the surface atoms of the metal. Fluorine, which has the highest electronegativity value, upon adsorption on iron leads to the greatest decrease in the electron work function, since among the adsorbates we have investigated it has the smallest ionic radius.

From the data obtained it follows^(1,2,4) that the temperature at which the greatest shift of the surface potential in the positive direction is observed is the lower, the smaller the radius of the ion of the adsorbates studied by us. This is apparently connected with the fact that adsorbate atoms, creeping under the upper layer of metal atoms to a certain distance, lead to the maximum decrease in the electron work function. In the case of fluorine this optimal distance, owing to the smaller value of the ionic radius, is reached at a lower temperature than in the case of the other electronegative gases. As the temperature is raised, the adsorbate atoms penetrate more deeply, and this leads to an increase in the electron work function.

Klemperer recently came to analogous conclusions, on the basis of literature data for oxygen, chlorine, bromine, and iodine⁽⁸⁾. According to his ideas, fluorine should lead to the greatest decrease in the electron work function, which is in agreement with our experimental data.

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