HOKKAIDO UNIVERSITY

— Review —

CHEMISORPTION AT GAS/SOLID AND SOLID/ELECTROLYTE INTERFACES

By

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Abstract

The investigation of the interaction of metals with oxygen is of great importance for elucidation of the mechanism of catalytic and electrochemical processes and corrosion of metals. Depending on the metal nature and the chemisorption conditions, the work function (W) can increase or decrease. This is defined by the adsorbate location on metal surface or beneath the surface layer of metal atoms.

The influence of chemisorbed oxygen on the work function of iron is compared with that of other electronegative gases (F, Cl, I).

It follows from the electric double layer theory at the metal/solution interface that the difference of the potentials of zero charge (pzc) of two metals is close to the difference in W of the metals in vacuum.

The results obtained show that the work function of the metals investigated in account of the influence the change of water vapors on W are in agreement with the value of W obtained from pzc.

In view of the progress in the studies on the surface properties of metals the interest in the gas chemisorption process and the influence of this process on the work function has greatly increassed.[1~5]

The Volta potential difference method was used for elucidation of the oxygen adsorption mechanism at solid/gas and solid/electrolyte interfaces.[4] These studies are of importence for investigation of the nature of catalytic and electrochemical processes and the corrosion mechanism of metals.

It follows from the theory of the electric double layer at the metal/solution interface developed by A. N. Frumkin[1,6~8] that the difference of the zero charge potentials (pzc) of two metals is close to the Volta potential difference of these metals in vacuum corresponding to the difference of their work function $\Delta W = W_1 - W_2$. In some cases this

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relation is approximate since it takes no account of the change in the surface potential of the metal caused by adsorption and orientation of water molecules[9], which is possible in electrochemical systems.

In the case of chemisorption of gases on metals the Volta potential difference depends on the adsorbate and adsorbent natures. In most cases gas chemisorption involves formation of a covalent partly ionic bond. The arising of the surface potential in this process is due to electron transfer from adsorbent to adsorbate or from adsorbate to adsorbent, which leads to increase or decresse of the work function, respectively. According to some authors[9,10] the sign of the surface potential of the metal $\Delta\varphi$ depends on the difference between the work function (W) and the electronegativity of adsorbate Ψ:

$$\Delta\varphi = W - \Psi$$

In this casse

$$\varphi = 1/2(I + E),$$

where I is the ionization potential and E is the affinity for electron.

In accordance with these concepts, the chemisorption of gases with a large affinity for electron, such as oxygen and halogens, should be accompanied by increase in the work function. However, it is known from[11,12] that oxygen chemisorption on certain metals can lead both to increase and to decrease the work function.

In order to investigate in more detail the chemisorption mechanism of gases on metals and their effect on electrochemical processes, e. g., passivity and corrosion of metals, a study was made of the influence of the chemisorption conditions and the nature of asorbates with different electron affinity (fluorine, oxygen, chlorine and iodine) on the work function.[13]

The studies on the influence of adsorbed gasses by the Volta potential difference method must be made on a clean metal surface.

The work function values available in literature for a number of metals differ greatly. The main reason of this discrepancy is different purity of metals and accuracy of measurements.

The work function can be determined by various methods, each of which has its limitations.[6]

The thermoelectronic method is used for homogeneous surfaces in particular separate crystal faces. On this account the mean work function of a polycrystalline surface measured from thermoemission can differ somewhat from the true work function of the metal.

The photoelectric method is used for determination of the work function both of separate crystal faces and polycrystalline surface. The spotted metal surface may affect the true work function values.[14~16]

More reliable results in determining the work function can be obtained by the

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Volta potential difference method. This method gives the mean work function values of the test specimen, but its accuracy depends mainly on the reliability of determining the work function of the reference electrode against which the Volta potential difference is measured.[17~20]

In the studies below the Volta potential difference was measured by the vibrating capacitor, photoelectric and thermoelectronic methods from the shift of the diode cha-racteristics. In the capacitor method (Fig. 1) a device was used in which a molybdenum plate with a thin glass layer soldered in to protect it from adsorption of gases[19] or a gold plate was used as a reference electrode. In this device measurements may be carried out under vacuum 10^{-10} Torr. In measurements by the thermoelectronic method as well, a device was used for cathode protection from gas adsorption on its surface.[12]
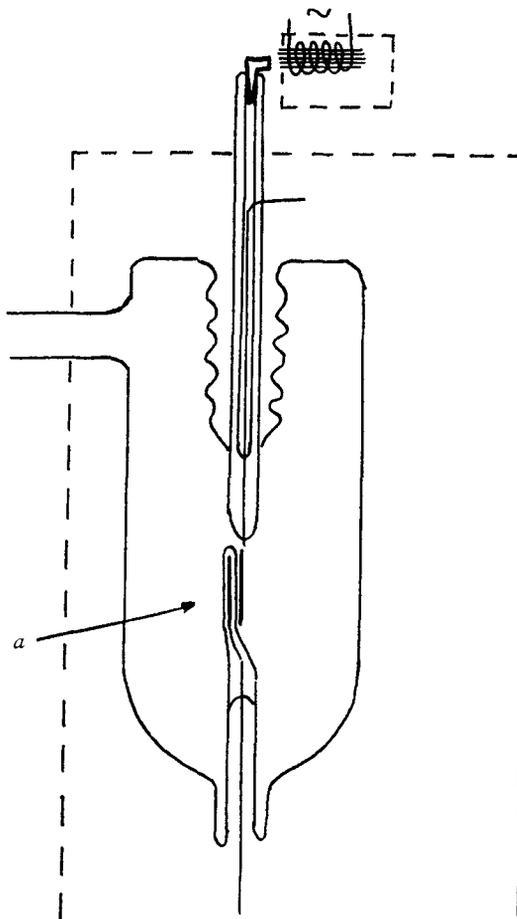

Fig. 1. Device for measuring the Volta potential difference.

The Volta potential difference values obtained for oxygen chemisorption on iron by the capacitor method[19] agree well with those obtained under the same conditions by the thermoelectronic method.[11,12]

As has been already mentioned, clean metal surface is of great importance for obtaining correct work function values. In some studies the work function was measured on evaportated films, single crystals and polycrystals using the above methods as well as the Auger and LEED spectroscopy.[21,22]

In view of the inhomogeneity of metal surface of interest are the data on the influence of the adsorbed oxygen amount on the metal work function. The most accurate data on polycrystals were obtained in the ΔW measurements by the VPD method with the reference electrode from molybdenum with soldered in glass.[19] This method was used for studying the influence of chemisorbed oxygen and water vapors on a number of metals (Hg, Ag, Pb, Fe, Ni, Pt, Ca. Ce). The metals investigated were multiply reduced in hydrogen at 450° and subjected to outgassing for long period of time at 700~900°C for Fe and Ni in vacuum. It was shown by special experiments that such treatment of Fe and Ni in vacuum 10^{-7} and 10^{-9} Torr does not result in an appreciable change of the Volta potential difference. Pt was outgassed at 1200° at 10^{-10} Torr and in the same conditions as Fe and Ni.

I. Gas/solid interface

Oxygen chemisorption on iron

In order to determine the dependence of the surface potential on the conditions of the interaction of electronegative gases with iron the Volta potential difference between clean metal surface and the surface covered by chemisorbed oxygen was measured.[11~13]

In studying the kinetics of oxygen chemisorption, iron surface was brought into contact with small oxygen portions at the pressure 5×10^{-2} Torr and the rate of adsorption of each portion (a/τ) was measured. The dependence of the oxygen adsorption rate on surface coverage is shown in Fig. 2 (Curve 1). Oxygen chemisorption on iron occurs in two steps. The fast step is characterized by a small change in the rate with surface coverage. Both for compact metal and powder, this step at 20°C ends when 2×10^{15} O_2 molecules chemisorbed per 1 cm². With further oxygen chemisorption the rate decreases sharply.[23~25] When iron with chemisorbed oxygen is heated no oxygen desorption occurs. However, after heating followed by cooling, iron is again capable of adsorbing oxygen (Fig. 2, Curves: 2—100°, 3—200°, 4—300°). Such activation of iron can be repeated many times. Thus the increase in the adsorbed oxygen amount at elevated temperatures is associated with the change in the structure of the oxide film formed at 20°.

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The results of the investigation of the interaction of iron with oxygen by the Volta potential difference method are given in Figs. 3, 4, 5. The data in Figs. 3 and 4 were obtained by the thermoelectronic method. Oxygen adsorption on iron in the amount 0.8×10^{15} mol/cm^2 at $-130°C$ leads to increase in the work function by 0.2 V (Fig. 3). However, when temperature rises to 100°C with the same amount of chemisorbed oxygen $(0.8 \times 10^{15}$ O_2 molecules per cm$^2)$ the work function decreases and is by 0.3 V less than for uncovered iron. When at 100°C the chemisorbed oxygen amount increases to 2×10^{15} O_2 molecules per cm^2 the work function decreases by 0.6 V $(-\Delta W)$. At larger chemisorbed oxygen amounts the work function increases (Fig. 4).
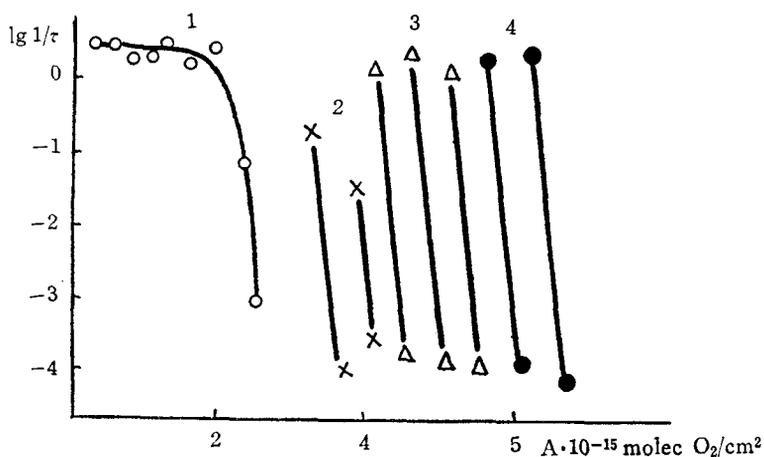

Fig. 2. Kinetics of oxygen chemisorption on iron. Curve
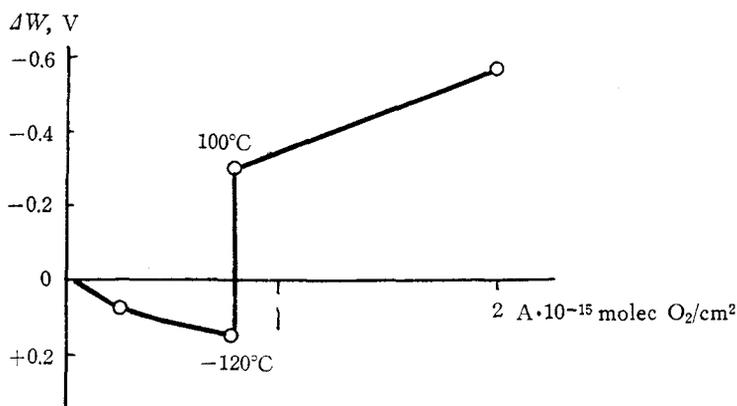1—30°C, 2—100°C, 3—200°C, 4—300°C.

Fig. 3. Influence of oxygen chemisorbed on iron on the work
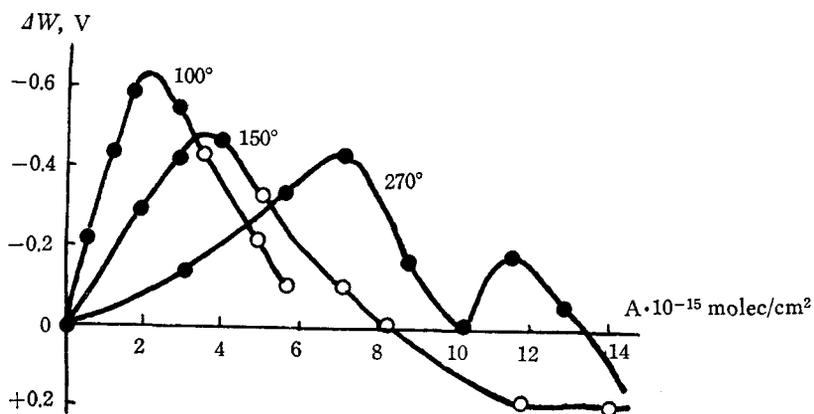function at $-120°C$ and 100°C.

ΔW, V

Fig. 4. Dependence of the work function of iron on the amount of adsorbed oxygen at 100°, 150°, 270°C.
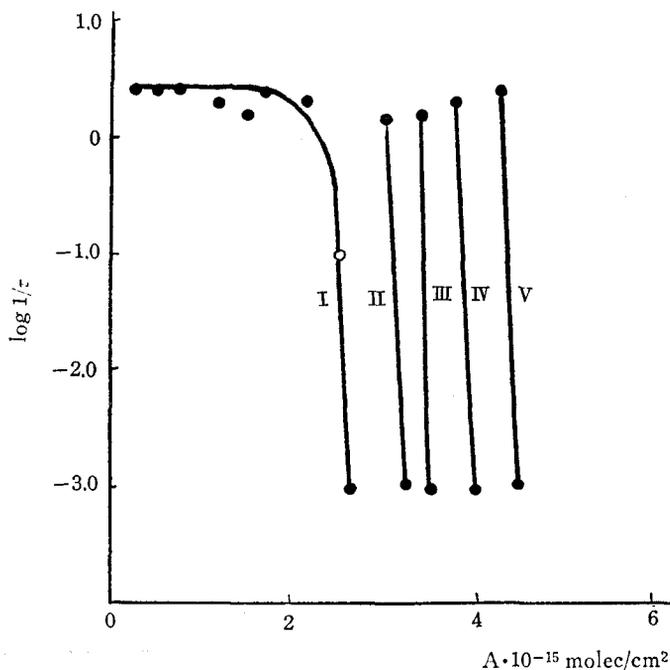

Fig. 5. Kinetics of oxygen chemisorption on iron and the influence of water vapors on oxygen chemisorption. $\lg \frac{1}{\tau}$ — the chemisorption time of different oxygen portions; A — the total amount of chemisorbed oxygen molecules/cm².

A similar dependence of the Volta potential on the amount of adsorbed O_2 is observed at 150° and 270° (Fig. 4). However, with rising temperature, the amount of quickly chemisorbed oxygen increases, but this leads to a lesser shift of the work function in the positive direction. As can be seen from Fig. 4, at O_2 amounts in excess of 8×10^{15} O_2 molecules per cm² at 150°C the work function is by 0.2 V greater than for reduced iron.

The results obtained by the capacitor method for iron with chemisorbed 2×10^{15} O_2 molecules per cm² support quantitatively the above results. At 100° the decrease in the work function is maximum, it is equal to 0.6 V.

As can be seen from Table 1, the most reliable work function value for iron is $4.7 \sim 4.8$ V.[26~28] The minimum work function of iron after chemisorption 2×10^{15} mol/cm² O_2 at 100°C is 4.1 V and the miaximum one 5.0 V after chemisorption at 150° 1.2 $\times 10^{16}$ mol/cm².

The Volta potential difference method was also used in investigating the mechanism of gas corrosion of iron in moist atmosphere.[25,28,29]

As has been pointed out above, oxygen chemisorption on iron at 20°C leads to

TABLE 1.

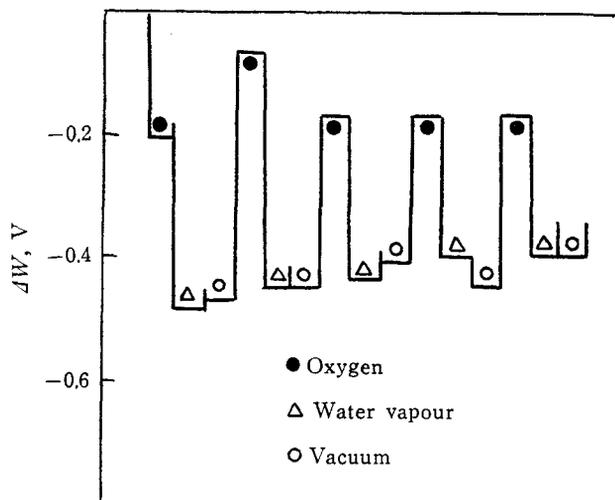| Metal	W	W+O_2	Ref.
Fe	4.70		26
	4.68		26
	4.71		27
	4.80	4.2	28
Ni	4.9		27
	5.09		27
	4.7	4.35	39

Fig. 6. Influence of oxygen and water vapors on the work function of iron.

decrease of the work function by 0.2 V. Upon contact with H_2O vapors the work function decreases further by 0.3 V. But after desorption of water vapors by prolonged outgassing, ΔW does not change. However, iron acquires the ability for further oxygen chemisorption. Such activation of iron with respect to interaction with oxygen can be repeated several times. As it follows from Fig. 5, oxygen chemisorption in the amount 2.5×10^{15} O_2 molecules per cm^2 leads to decrease in the oxygen chemisorption rate by about 3 orders (Curve 1). After treating iron covered with a limiting oxide film, with water vapors the rate of O_2 chemisorption again increases to the original value. However, upon further adsorption of a small amount of oxygen, the reaction rate decreases sharply and can be increased by subsequent treatment with water vapors (Curves 2, 3, 4 and 5, Fig. 5). The Volta potential difference values obtained for iron in the presence of oxygen, water vapors and after outgassing are given in Fig. 6. The comparison of the chemisorption measurements and the data on the influence of water vapors on the work function shows that the adsorption of H_2O vapors favors formation on metal surface of an electric double layer turned with its positive end outwards.

TABLE 2.

	Temperature (°C)	ΔW	O_2 mol/cm^2	ΔW fluorine		ΔW chlorine		ΔW iodine	
Fe	−120	+0,18	2.10^{15}						
	+ 20	−0,2	2.10^{15}	−0,65		+0,25		+0,55	
	+100	−0,6	2.10^{15}	−0,6	$P_{F_2} = 6.10^{-2}$ torr	+0,85	$P_{Cl_2} = 10^{-1}$ torr	+0,50	$P_{I_2} = 7.10^{-2}$ torr
	+200	−0,45	2.10^{15}	−0,5		+0,2		+0,35	
	+300	−0,25	2.10^{15}	−0,4		−0,1		−0,10	
	+100	−0,2	4.10^{15}						
	+150	−0,45	4.10^{15}						
	+300	−0,2	4.10^{15}						
Ni	+ 35	+0,1							
	+100	−0,4	$1,3.10^{15}$						
	+150	−0,17	$1,3.10^{15}$						
Pt	+200	+0,2	17.10^{15}	after 12 hours	$\Delta W = O$				
	+400	+1,5	125.10^{15}	after 12 hours	$\Delta W = O$				
	+800	+1,6	240.10^{15}	does not change					

Chemisorption of halogene on iron

Now let us consider the influence of other electronegative gases on the work function of iron.
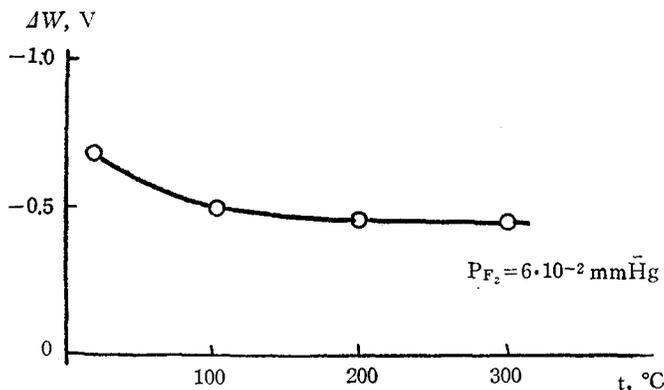
a) *Fluorine chemisorption on iron*

Fig. 7. Influence of fluorine chemisorbed on iron on the work function.

Especially marked is the decrease in the work function in the case of chemisorption of the most electronegative gas fluorine[31]. Fig. 7 shows the change in the surface potential of iron after its interaction with fluorine. Fluorine chemisorption was studied at the pressure 6×10^{-2} Torr. It follows from the obtained data that the maximum decrease in the work function in the case of fluorine chemisorption on iron is observed at room temperature and amounts to $0.6 \sim 0.7$ V, which corresponds to $W = 4.1 - 4.0$ V. This value does not change after fluorine removal from the gas phase. When with chemisorbed fluorine is heated under vacuum to $100°$ the work function increases somewhat. Further temperature increase to $300°$ practically does not affect the work function. Under these conditions W is by $0.4 \sim 0.5$ V less than for iron without chemisorbed flourine.

b) *Chemisorption of chlorine on iron*

The change in the surface potential of iron in the case of chlorine chemisorption was studied in the pressure range $4 \times 10^{-4} \sim 6 \times 10^{-1}$ Torr.[31~33] As it is evident from Fig. 8, heating iron with chlorine chemisorbed on its surface in the absence of chlorine in the gaseous phase results in considerable changes in its surface properties. At 100°C an increase in W from 0.1 to 0.85 V is observed over the pressure range indicated. With a further rise in the temperature, the work function decreases and after heating at 300°C becomes less by 0.1 V than for a clean iron surface. In the temperature range $20 \sim 100$°C at chlorine 5×10^{-2} Torr, the work function increases by $0.1 \sim 0.5$ V and at 6.1×10^{-1} by $0.3 \sim 0.85$ V. With further temperature increase the work function decreases and after heating at $300°$ becomes by 0.1 less than for uncovered iron surface.

c) *Iodine chemisorption on iron*

In order to determine the influence of iodine adsorbed on iron on the work function, experiments were made at the pressures 0.01 and 0.07 Torr.[35] These data are given
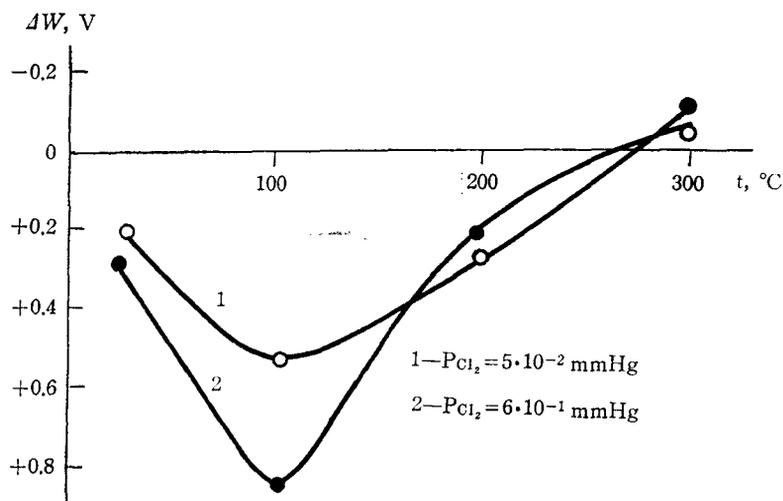
Fig. 8. Influence of chlorine chemisorbed on iron on the work function.
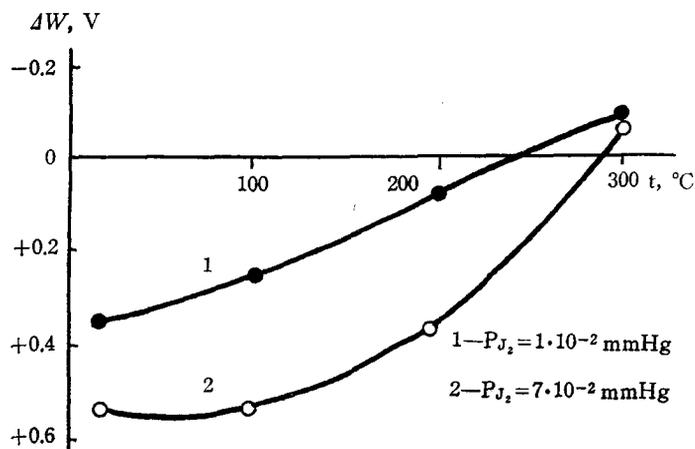

Fig. 9. Influence of iodine chemisorbed on iron on the work function.

in Fig. 9. Unlike the results obtained for chlorine, the maximum increase in the work function in the case of iodine chemisorption on iron is observed at 20°C. At the pressure 7×10^{-2} Torr the amount of chemisorbed iodine is 2.7×10^{15} I_2 molecules/cm² of true surface. After heating at 300° the work function is less by $0.1 \sim 0.15$ V that of clean iron surface. Unlike the results for chlorine, heating iron with chemisorbed iodine under vacuum leads to gradual decrease of the Volta potential difference.

As has been pointed out earlier, according to the generally accepted concepts, the adsorption on metal of oxygen and halogen, which have a great affinity for electron,

should be accompanied by increase in the work function. The data on oxygen chemisorption given above indicate that depending on the adsorption conditions (temperature and amount of chemisorbed gas), the work function may increase or decrease. The comparison of the data on the influence of oxygen and halogens, obtained at 20°C leads to the conclusion that the higher is the electronegativity of adsorbate, the less is the work function. The relationship between W and χ (electronegativity according to Pauling) is given by Curve 1 in Fig. 10. In Fig. 10 (Curve 2) the Volta potential difference values are confronted with the ion radii of the adsorbates investigated. It follows from these data that the value of the positive charge on the surface increases with decreasing ion radii.
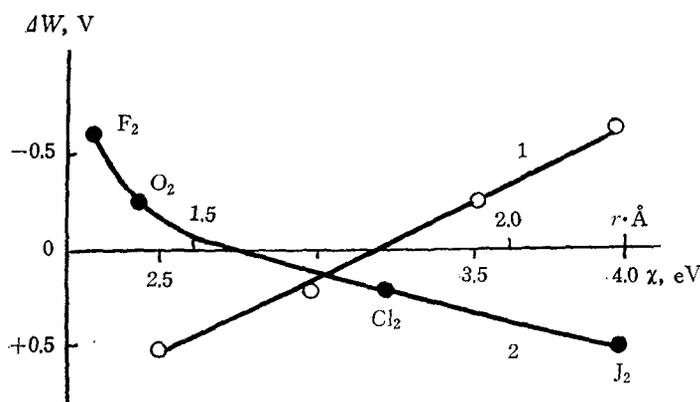

Fig. 10. Dependence of the Volta potential difference during chemisorption on iron of oxygen and halogens on the adsorbate electronegativity (Curve 1) and its ionic radius (Curve 2).

According to the concepts developed earlier[11~13,29] and those of Anderson[34] and Klemperer[36~37], the decrease in the work function in the case of adsorption of electronegative gases results from adsorbate penetration under the upper layer of metal atoms. The adsorbate ion size is of decisive importance for its penetration in between the surface metal atoms. It follows from the experiments that the adsorption at 20°C of fluorine, which has the smallest ion radius leads to the greatest decrease in the work function. Also the temperature at which the potential shift in the positive direction $(-\Delta W)$ is maximum is the higher, the less is the ion radius of the adsorbates investigated. The observed changes in the Volta potential difference with temperature can be explained by the following considerations. On iron the potential shift in the positive direction is caused by adsorbate penetration to some depth. Due to different ion radius values for the adsorbates studied this distance is reached at different *temperatures* (for fluorine at 20°C, for oxygen at 100°C, for chlorine and iodine above 300°). The positive surface potential decreases as oxygen penetrates into the depth of the metal.

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When penetration of electronegative adsorbates into iron or other metals is impossible, as is the case with chlorine (at 20°C), the surface is negatively charged $(+\Delta W)$. In the case of chlorine chemisorption on iron the temperature increase from 20 to 100° leads to further increase of the work function, which seems to be due to a change in the nature of the bond between chlorine and iron. In the temperature range above 100°C halogens may be formed on the surface, which is attended by a decrease of the negative charge.

It should be noted that the two forms of chemisorbed oxygen affect the electrochemical properties of iron in a different manner.[38,39] It was shown by the vacuum-electrochemical method that fast step of oxygen chemisorption increases the rate of anodic oxidation of iron, whereas the slow step decreases it.

Comparison of the data on the influence of chemisorbed oxygen on the work function[11,12] and on the electrichemical behavior of iron showed that the iron electrode activation is the result of O_2 chemisorption under the conditions causing decrease in the work function, whereas passivation is observed in the case of oxygen chemisorption accompanied by increase of the work function.

This problem will be discussed in more detail in Chapter 2.

Oxygen chemisorption on nickel and copper

The data on the oxygen adsorption on nickel (Fig. 11) and the influence of chemisorbed O_2 on the work function obtained[39,40] are very similar to those for iron. The same two types of adsorption: fast and slow are observed on nickel. At 20°C the fast step corresponds to 1.3×10^{15} O_2 molecules/cm². The comparison of these data with those obtained by the BET method gives the true surface of nickel on the carrier.[4]

As it follows from Fig. 11, at 35°C the fast chemisorption step leads to increase in the work function by 0.1 V. When the oxygen chemisorption temperature increases from 45 to 100°C the work function of Ni decreases by 0.02 and 0.35 V, respectively, as compared to reduced nickel, at 150°C the work function of Ni decrease by 0,15 V.

T. A. Delcher and F. C. Tompkins[4] studied oxygen adsorption on nickel surface obtained by metal vaporization under vacuum. Their results are in agreement with those of 39) and with the data obtained in the experiments on oxygen chemisorption on iron. It was shown in 42) that on vaporized nickel films, the decrease in the work function at 120°C is 0.7 V after prolonged exposure at this temperature. The authors of 42) explain this decrease by increase of the positive charge due to oxygen penetration under nickel surface layer.*) In 43) it was shown by the Leed method that the nickel surface layer with chemisorbed oxygen has a definite structure other than that of NiO. The decrease of the work function at 170°C on nickel chemisorbed oxygen was shown in 45).

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*) This shows the incorrectness of the statement of C. M. Quinn and M. W. Roberts[44] that the work function decrease was associated with the presence of hydrogen.
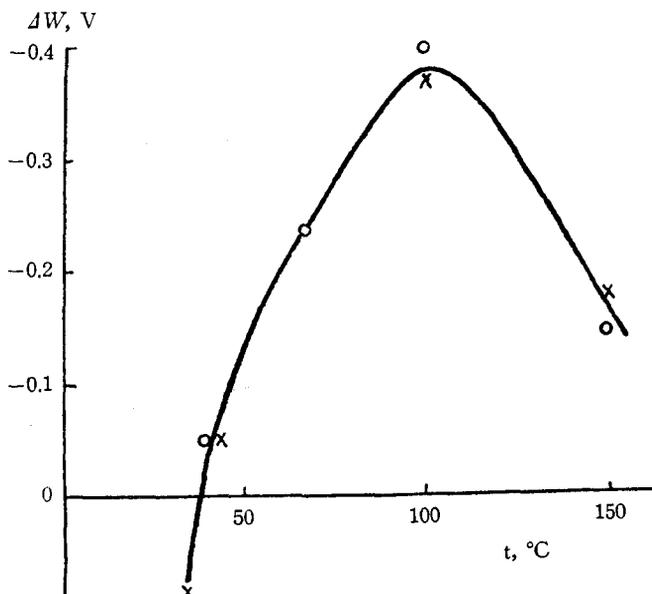
Fig. 11. Dependence of the work function of nickel on temperature at oxygen chemisorption$=1.3\times10^{15}$ molecules/cm².

Anderson and Klemperer[46,47] decided that change of work function at the chemisorption of oxygen on Ni at 20°C is a result of penetration of oxygen into the surface layers of metallic lattice.

The literature data on this problem are very controversial. According to Bosworth,[48] oxygen chemisorbed by nickel increases the work function by 1.4 V. According to Hunter[49] it decreases the work function by 1.08 V. Hackerman finds that at small oxygen pressures the work function of nickel decreases by 0.1 V.[50] Apparently, the discrepancy in the results can be explained by different chemisorbed oxygen amounts and different temperatures at which chemisorption was carried out.

The kinetics and mechanism of chlorine adsorption on sprayed nickel films were studied by Anderson[51] in the pressure range $5\times10^{-6}\sim5\times10^{-3}$ Torr at 20 and -122°C. Under these conditions until a monolayer coverage is reached chlorine adsorption occurs very fast. At low coverages $(\theta=0.1)$ the work function decreases by 0.2 V, which Anderson explains by the chemisorbed chlorine location under the metal surface layer.

Hofman *et al.*[52] studied the influence of chemisorbed oxygen on the work function of copper. The measurements in the temperature range $20\sim450$°C showed that at room temperature the work function of copper during oxygen chemisorption increases by 330 mV. At higher temperatures the work function decreases significantly (Fig. 12).
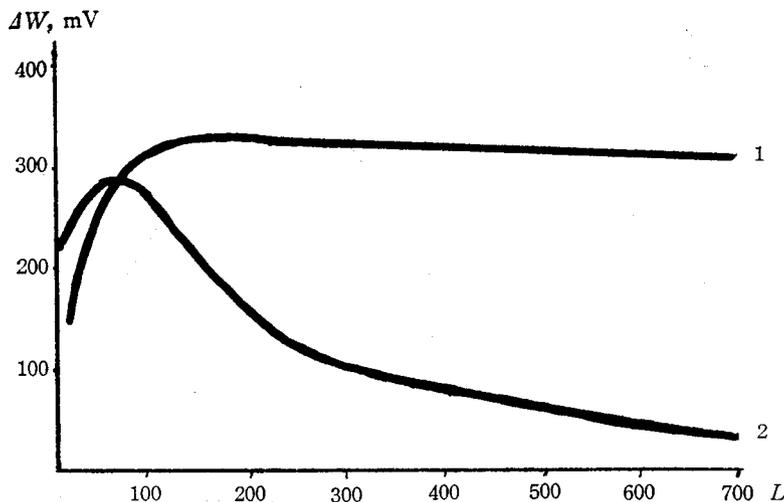
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Fig. 12. Dependence of the work function of copper on oxygen chemisorption: 1—for 20°C, 2—for 200°C. L-oxygen exposure (Langmuir).

At 200°C it decreases by 300 mV. The work function decreases the more, the longer oxygen remains on the copper surface. These data are similar to the relevant data for iron and nickel. As shown by Hofman, the decrease of the work function of copper with varying temperature is associated with the change in the surface layer structure.

Oxygen chemisorption on platinum

For platinum the influence of oxygen adsorption on the work function is different. The work function of platinum outgassed under high vacuum at $P = 10^{-10}$ Torr and the outgassing temperature 1200°C is determined by the photo effect method $W = 5.6$ eV.[41] The results obtained in the studies on the chemisorption of oxygen, hydrogen and water vapors on such platinum are given on Fig. 13. It follows from these data that oxygen chemisorption at 23°C and $P = 10^{-4}$ Torr increases the work function by 0.6 V. However, with time under vacuum the work function decreases and becomes close to that of outgassed platinum. Hydrogen adsorbed on platinum previously outgassed under vacuum 2×10^{-10} Torr decreases the work function by 0.15 V. Adsorption of water vapors leads to decrease of the work function at $P = 5 \times 10^{-5}$ Torr equal to $0.6 \sim 0.7$ eV in 10 minutes. Removal of water vapors from the gas phase does not affect the work function.[53] When the pressure of water vapors is increased to 5 Torr the work function decreases by 0.9 V and is equal to 4.8 V. However, platinum outgassed at 900°C and under vacuum 10^{-8} Torr measured by the VPD method[54] has the work function 4.65 V. On such platinum oxygen adsorption at $P = 0.1$ Torr and 20°C is insignificant and the work function does not change. In the range $200 \sim 800$°C outgassed platinum

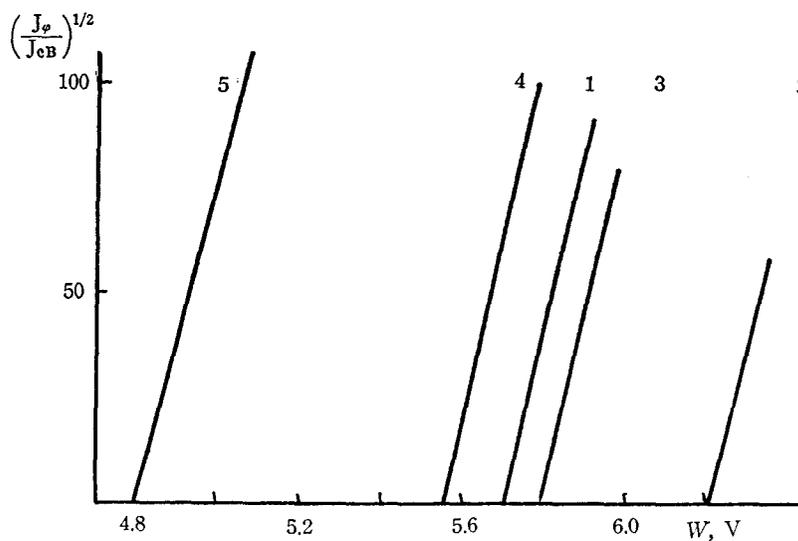$$\left(\frac{J_\varphi}{J_{cB}}\right)^{1/2}$$

Fig. 13. Fowler curves 1—platinum outgassed at 1200°C and $p = 10^{-10}$ Torr; 2, 3—10 and 120 min after O_2 adsorption at $p = 10^{-4}$ Torr, respectively; 4—after H_2 adsorption at $p = 10^{-5}$ Torr; 5—after adsorption of water vapors.

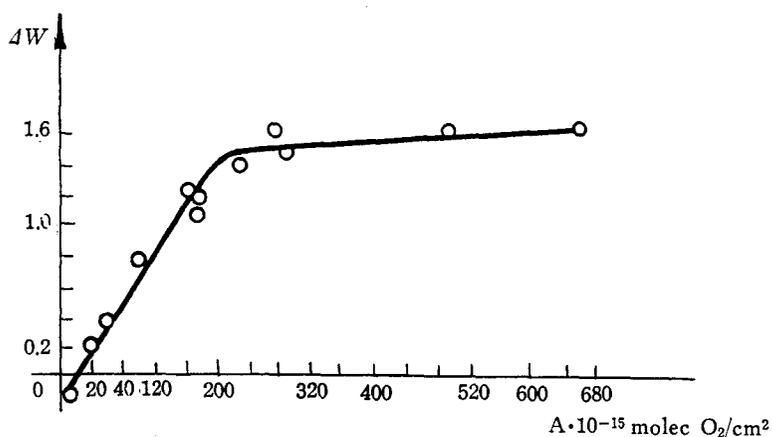**Fig. 14.** Influence of the chemisorbed oxygen amount at 800°C on the work function of platinum.

can adsorb considerable of oxygen amounts, corresponding to 600 monolayers at 800°C (Fig. 14).

On platinum with oxygen adsorbed in the amount $15 \times 10^{15} \sim 40 \times 10^{15}$ O_2 molecules/ cm² at 200°C, the work function increases (0.2 V), this increase disappearing if the electrode is kept under vacuum during 12 hours.[55] In this case the work function of platinum practically coincides with that for uncovered metal. This can be explained by oxygen penetration into the depth. In the case of chemisorption at 400°C the same amount of oxygen (40×10^{15} O_2 molecules/cm²) does not affect the work function at all. This phenomenon seems to be associated with the fact that oxygen penetrates so fast into the depth of the metal that it is impossible to measure it by the VPD method.

However, with increasing of adsorbed oxygen amount at 400°C the layers adjoining the platinum surface become covered and oxygen penetration into the depth of the metal slows down. Large amounts chemisorbed oxygen of the order of $100 \times 10^{15} \sim 200 \times 10^{15}$ O_2 molecules/cm² lead to increase of the work function by 1.5 V. But the Volta potential difference decreases with time, and after 12 hours the work function becomes equal to that of uncovered platinum, which, as in the cases described above, is associated with oxygen penetration into the depth of the metal (Fig. 15). Quite different is the behavior of oxygen adsorbed by platinum at 800°C. The results of measurements of a set of experiments are shown on Fig. 14. An increase in the chemisorbed oxygen amount leads to increase of the work function and practically does not change with time. When 233×10^{15} O_2 molecules/cm² have been adsorbed ΔW is 1.5 V. Further oxygen chemisorption practically does not affect the work function. The obtained results indicate that a small part of chemisorbed oxygen is strongly bound with the metal
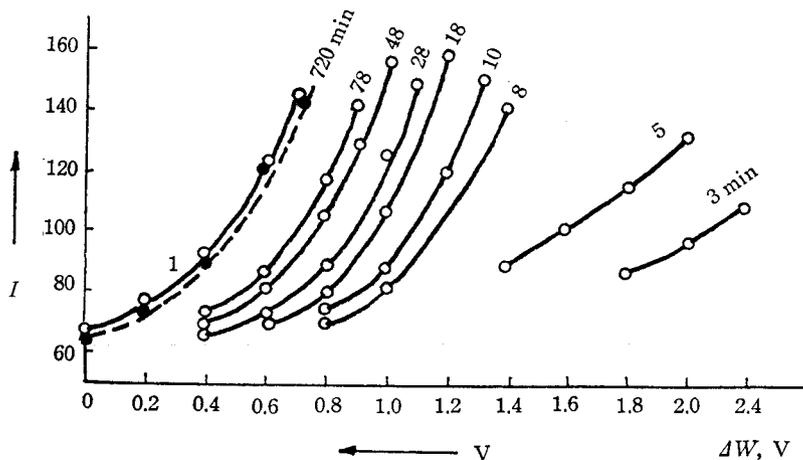

Fig. 15. Change in the work function of platinum$+125 \times 10^{15}$ O_2 molecules/cm² with time varying from 3 to 720 min.
I-the current of electron emission (relative units)

surface while the major portion of O_2 penetrates into the depth of the metal.

Oxygen chemisorption on rhodium

To obtain clean surface, rhodium was multiply reduced in hydrogen at 400°C and then outgassed at 900°C under vacuum 10^{-8} Torr during $10 \sim 50$ hours. Oxygen adsorption on rhodium plates thus cleaned[56] increases considerably in the temperature range $23 \approx 400$°C. At 20°C oxygen chemisorption corresponds to the surface coverage equal to 0.5 and at 400°C, to 1.5 oxygen monolayers. As can be seen from Fig. 16 for rhodium, the increase in the work function due to adsorbed oxygen is as follows: at 23°C by 0.45 V, at 100°C by 0.68 V, at 200°C by 0.95 V, at 300°C by 1.05 V, at 400°C by 1.5 V.
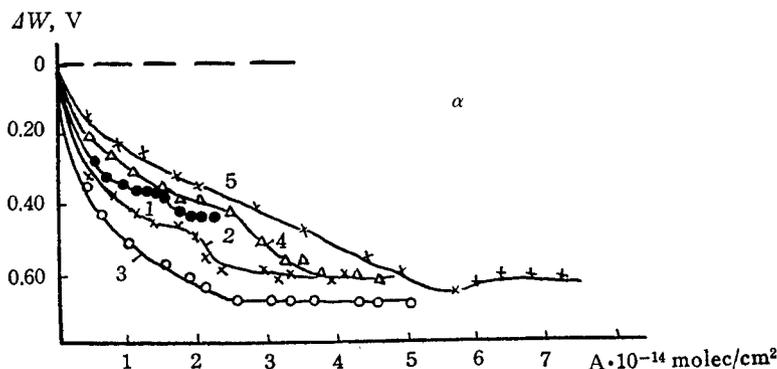

Fig. 16. Dependence of the work function of rhodium on the chemisorbed oxygen amount at t°C: 1—23, 2—100, 3—200, 4—300, 5—400.

Oxygen chemisorption on silver

The influence of chemisorbed oxygen on the work function of silver was studied in 57 ~ 59) Both fast and slow chemisorptions are observed on silver surface in the temperature range $20 \sim 400$°C. As can be seen from Fig. 17, the oxygen amount adsorbed during the fast step in this temperature range rises from 0.25 to 0.6 monolayer. The work function of silver was studied by different methods. Oxygen chemisorption at 20°C during the fast step increases the work function by 0.45 V. When the chemisorption temperature rises to 200°C, the work function increases by 0.7V. At 200°C the amount of quickly adsorbed oxygen is equal to adsorbed slowly. According to Temkin *et al.*, under these conditions surface layers of Ag_2O and AgO are formed.[59]

When silver is heated to 400°C under vacuum, no oxygen desorption occurs, but silver acquires the ability of adsorbing additional oxygen amounts. This fact points to oxygen penetration into the metal depth. The work function of clean surface, reduced and outgassed under vacuum at 10^{-8} Torr is $4.1 \sim 4.2$ V. The work function of silver
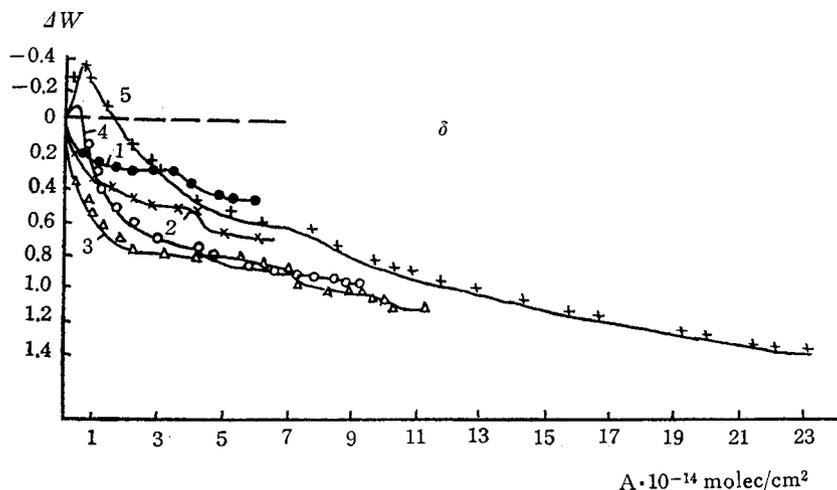
Fig. 17. Dependence of the work function of silver on the chemisorbed oxygen amount at t°C: 1—23, 2—100, 3—200, 4—300, 5—400.

surface covered by quickly adsorbed oxygen is 4.5 ~ 4.6 V. Desorption of water vapors does not affect the work function of silver. The descrepency in the data (for Ag) is mainly associated with different methods of the work function measurements and with different cleanness of silver surface.

Work function of mercury and lead

The work function values for mercury available in literature show good agreement. According to the measurements carried out,[65] the work function of Hg (the mean of a large number of measurements) is equal to 4.48 ± 0.02 V. It is shown in 61 ~ 63) that on mercury water is adsorbed at low pressures. According to 64, 65) water adsorption on mercury starts at $P/P_s = 20\%$ and 40%, respectively. It is show in 65) that in the whole H_2O pressure range studied (1-80%) the Volta potential varies within ± 0.03 V, which virtually coinsides with the accuracy of measurement. These values agree with Low's data,[66] who showed that at $P/P_s - 40\%$, the Volta potential $\Delta W_{Hg+H_2O} - \Delta W_{Hg}$ does not exceed 0.05 V.

The work function of lead measured by the Volta potential difference method under vacuum 10^{-7} Torr is equal to 4.05 V,[67] which by 0.05 V exceeds the value obtained by Andersen and Hunt[68] by the same method (4.0 V). The values of measured by the external photoeffect and the thermoionic emission methods are 4.15 and 4.00 V, respectively. Water vapors practically no effect on the work function of lead.

Work function of gallium

There are very few data on the work function of gallium in literature. The work

function of gallium measured under ultra vaccum by the Volta potential difference method is equal to 4.39 V, which is in good agreement with the value found by S. D. Levina and Z. A. Rotenberg.[69]

Water vapors cause both an irreversible and a reversible change of the work function of gallium.[70] At $P/P_s = 70\%$ the total decrease of the work function is 0.28 V. After removal of water vapors from the gas phase ΔW is equal to 0.09 V.

II. Influence of chemisorbed oxygen at the metal/electrolyte interface

Potential of zero charge

The determination of the zero charge potential of metals gives an answer to the question of the relation between the emf of a galvanic cell and the Volta potential of these metals in the absence of chemical interaction.

The difference of the potentials of zero charge ($\varphi_{s=0}$) corresponds to the difference of potentials of these metals in vacuum (ΔW). Here the difference of potentials of the ionic double layers at the metal/electrolyte interface is eliminated, but the metal surface in vacuum is substituted by the metal surface in contact with electrolyte solution.

It is known that $\varphi_{s=0}$ can be measured by several methods. For measuring the potential of zero charge of mercury and other metals in liquid state the electrocapillary curves and the differential capacity methods are used.

For metals in solid state not adsorbing hydrogen (Ag, Ga, Pb) the differential capacity method is used and for those adsorbing hydrogen (Pt, Rh) the differential capacity method, the radioactive tracer technique and the charging curves method.

TABLE 3.

Metal	pzc $\varphi_{s=0}$	Electrolyte	Method	Reference
Hg	−0.19	0.01 N NaF	Capacity minimum electrocapillary	71 72
Ag	−0.7	0.001 N Na$_2$SO$_4$	Capacity minimum	73
Pb	−0.56	0.001 N NaF	Capacity minimum	74
Ga	−0.69	1 N NaClO$_4$+1 N HClO$_4$	Electrocapillary Capacity minimum	75 76
Fe	−0.7	0.005 N H$_2$SO$_4$	Capacity minimum	77
Pt	+0.185	0.1 N KF+0.3 N HF	Ion adsorption	78

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The data on the potential of zero charge of some metals are given in Table 3.

In comparing the difference of the work function of metals and the difference of the potentials of zero charge of these metals, account should be taken of the change in the work function due to adsorption of water vapors. The data on the influence of water vapors on the work function are given in Table 4.

Table 4.

Metal	Work function W eV[*]	pzc $\varphi_{s=0}$	ΔW_{H_2O}	H_2O torr	W Me pzc	$W - \Delta W_{H_2O}$
Hg	4.50	$-0.19+0.01$	0.0	14	4.50	4.50
Ag	4.0	-0.7	0.0	12	3.99	4.0
Pb	4.05	-0.56 ± 0.02	0.0	12	4.13	4.05
Ga	4.39	-0.69 ± 0.01	0.28	14	4.0	4.11
Fe[**]	4.72	$-0.7\ \pm0.05$	0.60	10	3.99	4.12
Pt	5.7	$0.18+(pH\,2)$	0.9	10^{-4}	4.87	4.8

*) The accuracy is ±0.03 V.
**) The mean value of Table 1.

Water vapors do not affect the work function of mercury, silver and lead. Since very reliable data on the work function of mercury and its potential of zero charge are available, these quantities have been compared with the use of the equation:

$$W_m = W_{Hg} - (\varphi_{s=0}^m - \varphi_{s=0}^{Hg})$$

The work function of mercury $W = 4.48$ and $\varphi_{s=0} = -0.19$ V. The data on the work function obtained from the potentials of zero charge and by the VPD method are given in Table 4.

It follows from these data that for lead and silver the data obtained by the two methods used show good agreement. In comparing the corresponding data for gallium, whose work function is 4.39 V with the potential obtained from pzc, we see that in the pressence of water vapors, the work function of gallium is by 0.28 V less than the value obtained in vacuum and is equal to 4.11 V, which by 0.11 V differs from the data obtained from pzc. However, in accordance with the concepts developed for gallium, it would be more correct to compare the differences of the work function of mercury and gallium and the differences of electrochemical potentials of this metals at the negative surface charge,[76] which is equal 0.17 V and correspond W pzc = 4.33.

The work function of Pt measured by the photoelectric method under ultravacuum (10⁻¹⁰ Torr) is 5.7 V. Under these conditions the work function may be influenced by the spotted surface and therefore it would be expedient to compare the potential of zero charge with the work function value of Pt obtained in the presence of water va-

pors. In this case the work function of Pt is 4.8 V and W pzc = 4,87. In the case of iron the difference of work function calculated from pzc and allowing for the change of W due to water vapors is 0.12 V.

The results obtained for the metals shown in Table 4 are in satisfactory agreement with the theory of the electric double layer of the metal — solution interface.[1]

Activation and passivation of metals by oxygen

It was shown in the studies on the influence of chemisorbed oxygen on the properties of metals in electrolyte solutions that depending on the chemisorption conditions, metals can undergo activation and passivation. Iron electrode, reduced by hydrogen and outgassed under vacuum by a method similar to that used in determining the influence of oxygen on the work function, were brought into contact with outgassed alkaline solution, where-upon the influence of chemisorbed oxygen on the shape of anodic and cathodic polarization curves was examined. For investigation of gas adsorption by
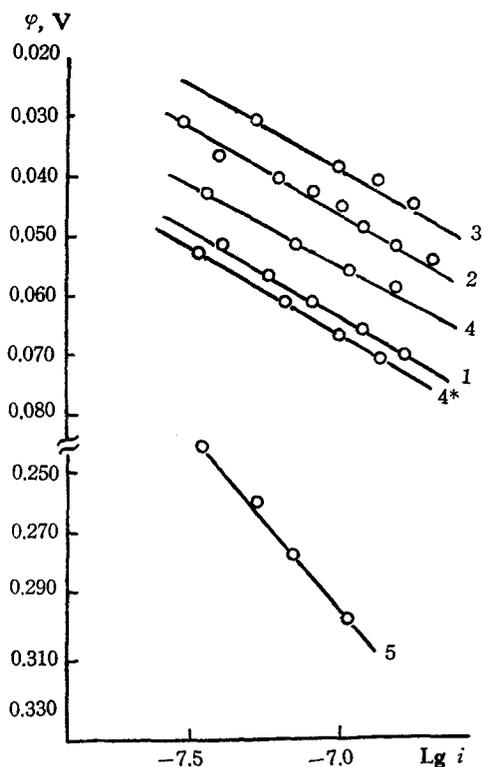

Fig. 18. Influence of oxygen adsorbed by iron on the shape of the polarization curves. 1—uncovered iron, 2, 3, 4, 5—iron with 0.6×10^{15}, 0.9×10^{15}, 2×10^{15}, 3.5×10^{15} O_2 molecules/cm², 4*—change of Curve 4 with time.

an electrochemical method a device was used, described in 79) which made it possible after chemisorption to bring the adsorbent into contact with outgassed electrolyte solution and to study the electrochemical characteristics.

The results of the studies on the influence of oxygen chemisorbed on iron on the shape of the anodic curves in 0.25 N NaOH solution are given in Fig. 18. It is clear from these data that when the amount of chemisorbed oxygen on the surface of outgassed iron increases, the anodic curves at first shift in the direction of more negative potentials, which points to electrode activation. With further increase of the oxygen chemisorption the anodic polarization curves shift in the direction of more positive potentials and iron undergoes passivation. The potential shift in the negative direction at the amount of chemisorbed oxygen equal to 0.9×10^{15} molecules/cm^2 is 25 mV, which correspond to a seven-fold increase in the anodic process rate. When 3.3×10^{15} molecules/
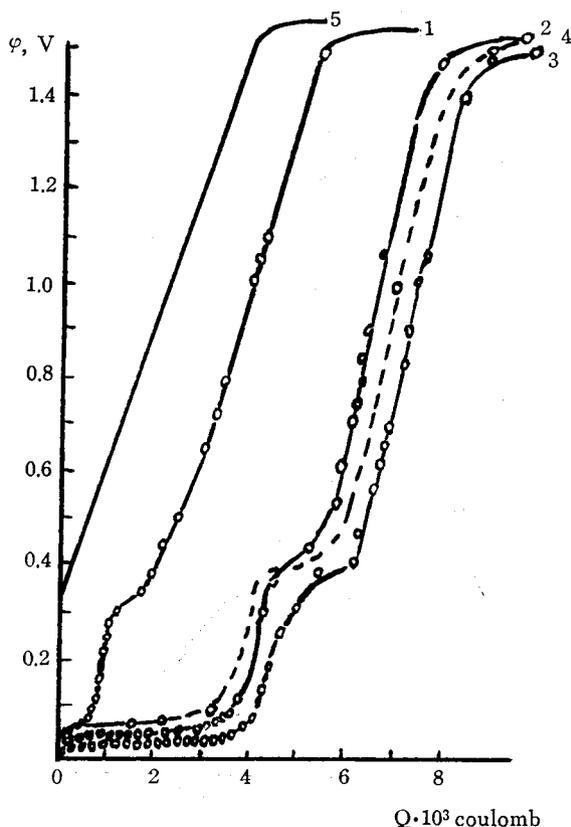

Fig. 19. Dependence of the electrochemical process efficiency on potential. 1—uncovered iron; 2, 3, 4, 5—iron with 0.6×10^{15}, 0.9×10^{15}, 2×10^{15}, 3.3×10^{15} O$_2$ molecules/cm^2.

cm² have been adsorbed, the polarization curves shift in the positive direction by 200 mV that corresponds to passivation. The electrode activation by small chemisorbed oxygen amounts was also studied by measuring the dependence of the potential corresponding to Fe(OH)₂ formation on the amount of passed electricity Q. The results of the experiments carried out at the current density 1.4×10^{-7} A/cm² are shown in Fig. 19. It is clear from the Figure that in 0.25 N NaOH solution in the presence of 0.9×10^{16} O₂ molecules/cm² on the surface, the electrochemical process efficiency increases $6 \sim 7$ times as compared with that on clean iron. The chemisorption 3.3×10^{16} molecules/cm² bring to complete passivation of the formation Fe(OH)₂.

In order to elucidate the mechanism of iron activation and passivation by gaseous oxygen a study was made of the impedance of an iron electrode as affected by potential and the amount of adsorbed oxygen. Fig. 20 shows the dependence of capacity on potential during anodic polarization in 0.28 N NaOH for an iron electrode. Curve 1 is for an uncovered iron electrode. Curve 2 is for an iron electrode with 1.1×10^{16} chemisorbed O₂/cm².[79~82]

It follows from the obtained data that when 1.1×10^{16} O₂ molecules/cm² are chemisorbed from the gas phase on the iron surface the capacity of the iron electrode increases significanty at the potential corresponding to formation of Fe(OH)₂. When the adsorbed oxygen amounts increases further to 2×10^{16} molecules/cm², the capacity does not change.

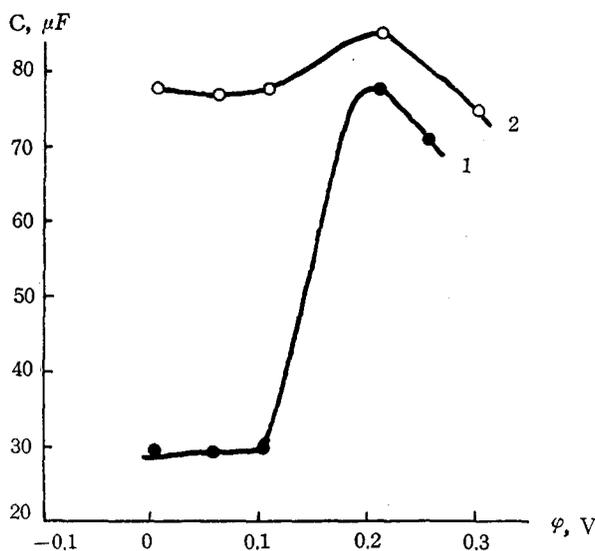The mechanism of iron passivation and activation by oxygen is associated with

Fig. 20. Dependence of capacity (C) on potential. 1—uncovered iron, 2—iron with 2×10^{15} O₂ molecules/cm².

mechanism of the primary stage of oxygen chemisorption.

The studies on the mechanism of iron passivation by oxygen carried out by the Volta potential difference method have led to establishment of the relationship between the work function and the electrochemical behavoir of the electrode. Small amounts of chemisorbed oxygen decrease the work function of iron, increase the anodic process rate and decrease the self-discharge of iron electrodes.

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