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EFFECT OF CHEMISORBED GASES ON THE WORK FUNCTION OF METALS

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Most of the work on the mechanism of the adsorption and chemisorption of gases on metals has been concerned with the kinetics of these processes and with the relevant heats of adsorption. Yet, attempts were made as long ago as in the 1930's to establish a connection between the rate of interaction of gases with metals and the change in work function of the metals.

Rideal and his coworkers [1] studied the relationship between the activation energy and the work function. Langmuir [2], de Boer [3], Lukirskii [4], and others, measured the change in contact potential difference (c.p.d.) resulting from the adsorption of alkali metal atoms on tungsten, and from the adsorption of oxygen and hydrogen on alkali metals. However, the literature of that period contains various contradictory results as well as some very valuable papers: this state of affairs, which was due to the inadequacy of existing measurement techniques, was responsible for the loss of interest in this problem. In recent years, modern theories of gas–metal interactions and the development of high-vacuum and electronic measurement techniques gave new impetus to studies of the mechanism of the adsorption of gases on metals and of their influence on the work function. Recent investigations include the effect of the adsorption of hydrogen, oxygen, carbon monoxide, the noble gases, etc., on the work function of metals, and some attempts at establishing the relation between the changes in work function and in heat of adsorption under conditions of increasing surface coverage [5,6].

The results of work function measurements as a function of gas adsorption were used by several workers to calculate heats of adsorption. Eley [7] suggested the use of a semi-empirical formula, based on Pauling's equation for the energy of a covalent bond:

$$-\Delta H_0 = H_c + 23.06\,(x_m - x_a)^2, \qquad (1)$$

where H_C is the initial energy of the covalent bond, and $(x_m - x_a)$ is the electronegativity difference between the adsorbent and the adsorbate.

Calculations of the heat of adsorption of hydrogen chemisorbed on tungsten, using this equation, agree satisfactorily with experimental data. However, the adsorption of oxygen, nitrogen, and also some organic molecules gave appreciable discrepancies between calculated and experimental values. Eley's calculation presupposes a linear change of contact p.d. with surface coverage, which is not always borne out by the experimental results.

The contact p.d. method has been used also to examine the mechanism of catalytic and electrochemical processes.

Work function values are of major significance [8,9] in problems involving the Volta potential, which, according to the ideas developed by Frumkin, determines the relation between the points of zero charge of metals and their work functions.

The contact potential difference in the chemisorption of gases on metals depends on the nature of both the adsorbent and the adsorbate [5,6,10]. In most cases, chemisorption of gases produces a covalent bond of partially ionic character. Under these conditions, the appearance of a surface potential is associated with the transfer of an electron from the adsorbent to the adsorbate or *vice versa*. These processes lead to an increase or a decrease in the work function respectively. According to the ideas of a number of workers [5,6,10], the sign of the surface potential of the metal, $\Delta\varphi$, is determined by the difference between the work function (φ) and the electronegativity of the adsorbate (ψ):

$$\Delta\varphi = \varphi - \psi. \qquad (2)$$

Hence

$$\psi = {}^1/_2(I + E), \qquad (3)$$

where I is the ionisation potential and E is the electron affinity.

This model predicts that chemisorption of gases having a high electron affinity, such as oxygen and the halogens, should raise the work function. Yet even some of the earlier work[11-14] showed that oxygen chemisorption on certain metals raises φ while according to others chemisorption lowers it.

The influence of chemisorption conditions and of the nature of adsorbates of different electron affinity (fluorine, oxygen, chlorine, iodine) on the work function has been investigated as part of a detailed study of the mechanism of the chemisorption of gases on metals and of their effect on electrochemical processes such as metal passivation and corrosion.

In most of the published studies of chemisorption processes by the contact potential difference method no allowance is made for the change in surface potential of the reference electrode induced by the adsorbate.

The measurements of contact p.d. in our work were made by the vibrating condenser method and by the thermionic method (from the change in diode characteristics). For the condenser method we used an apparatus in which the reference electrode was a molybdenum sheet fused to a thin layer of glass, which protected the reference electrode from gas adsorption[15]. When the measurements were made by the thermionic method, we used an apparatus which enabled the cathode to be protected from adsorption of the experimental gases[16]. The values of contact p.d. obtained for oxygen chemisorption on iron by the condenser method[17] are in good agreement with our own results by the thermionic method under similar conditions[16,18].

The preparation of a clean metal surface is a very complicated problem. The usual procedures are either cleaning of the metal surface by reduction with carbon monoxide, followed by lengthy degassing in an ultra-high vacuum, or evaporation of the metal in an ultra-high vacuum. In the second method there is a possibility of absorption by the evaporating metal of the gases evolved from the massive metal. Furthermore, the structure of thin films is different from that of bulk metal, and this can affect the work function[19-23]. For these reasons we used the first method in our researches.

The metals were reduced at 450° and degassed at 700–900° (iron[17,18] and nickel[24]), or at 1200° (platinum[25]). Special experiments were made to check that when this procedure was used, a change in vacuum from 10^{-7} to 10^{-9} mmHg had no significant effect on the change in contact p.d. caused by oxygen chemisorption[26].

Vacuum work with halogens presents considerable difficulty. To ensure that the gases were pure, we used spherical diaphragms instead of taps[27,28].

The chemisorption of oxygen on tungsten is a classical example showing the correctness of the above ideas on the change in work function in terms of the difference in electron affinity between adsorbate and adsorbent. Both published results[29-32] and measurements in our own laboratory[16] have shown that the work function of tungsten is decreased by oxygen chemisorption over a wide range of pressures and temperatures. In most of the investigations, made by different methods, the contact p.d. $\Delta\varphi$ is found to be 1.7–1.9 V.

In order to understand the variation of the surface potential with the conditions of interaction of electronegative gases with iron, we measured the contact p.d. between a clean metal surface and a surface covered with chemisorbed gases.

To study the kinetics of oxygen chemisorption, an iron surface was exposed to small increments of oxygen pressure, and the rate of absorption of each portion was observed. The variation of the rate of oxygen absorption with surface coverage is shown in Fig. 1 (curve *1*), where the rate of the process is expressed as $\log(1/\tau)$ and τ is the time required for absorption of one-half of the aliquot of oxygen. The chemisorption of oxygen on iron occurs in two stages. The fast stage is characterised by relative insensitivity of the rate to the degree of surface coverage. This stage is completed, both for the bulk metal and for the powder, when the extent of absorption is 2×10^{15} O_2 molecules per cm² of true surface area. If absorption is allowed to proceed further, the rate of chemisorption falls off sharply[33,34]. No desorption occurs upon heating iron covered with chemisorbed oxygen. However, after being heated and subsequently cooled, iron acquires the ability to absorb additional oxygen [see Fig. 1, curve *2* (100°), curve *3* (200°), curve *4* (300°)]. This activating treatment of the iron can be repeated a number of times. Thus, the increase in oxygen absorption at higher temperatures stems from disruption of the protective properties of the film formed at 20° As the temperature is increased, the limiting thickness of the film also rises, and additional chemisorption of oxygen must take place[17].

The results of our work on the interaction between iron and oxygen by the contact p.d. method are shown in Figs. 2, 3, and 4. The data of Figs. 2 and 3 were obtained by the

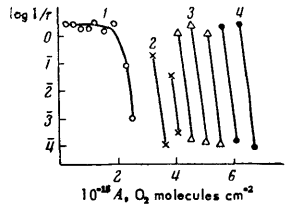


Fig. 1. Effect of temperature on the kinetics of oxygen chemisorption on iron.

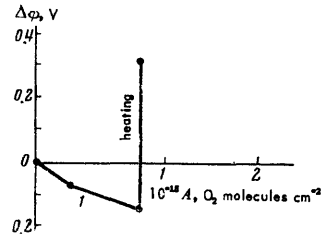


Fig. 2. Effect of oxygen, chemisorbed on iron at -120° and 100°, on the contact p.d.

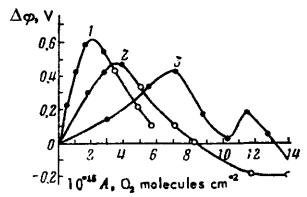


Fig. 3. Variation of contact p.d. of iron with amount of oxygen chemisorbed: 1) at 100°; 2) at 200°; 3) at 300°.

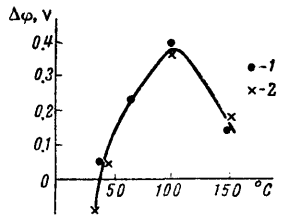


Fig. 5. Effect of temperature on the contact p.d. of nickel covered with 1.3×10^{15} O_2 molecules cm^{-2}. Points 1 and 2 refer to different experiments.

thermionic method. Adsorption of oxygen on iron at -120° raises the work function (Fig. 2), in agreement with the ideas discussed above. However, when the temperature is increased to 100° for the same amount of chemisorbed oxygen (0.8×10^{15} O_2 molecules per cm^2), the work function decreases to a level 0.3 V lower than for clean iron. If the amount of chemisorbed oxygen is increased to 2×10^{15} O_2 molecules per cm^2, the work function drops by 0.6 V. When the extent of oxygen chemisorption is very high, the work function increases (Fig. 3).

A similar variation of contact potential with amount of absorbed O_2 is found at 150° and 270°. However, the work function minimum shifts towards higher coverages by chemisorbed oxygen as the temperature of chemisorption is increased. As Fig. 3 shows, the work function becomes 0.2 V higher than that for reduced iron when the amount of O_2 exceeds 8×10^{15} molecules per cm^2.

Experimental results[17] obtained by the condenser method with iron covered to the extent of 2×10^{15} O_2 molecules per cm^2 are in quantitative agreement with the results given above. At 100° the decrease in work function goes through a maximum of 0.6 V (Fig. 4).

Since the most reliable value[35] for the work function of iron is 4.7 V, which agrees with our own measurements, the lowest work function of iron in the presence of O_2 absorption is 4.1 V, and the highest is 4.9 V.

Our results for the adsorption of oxygen on nickel and for the influence of chemisorbed O_2 on the work function show much the same features as the results for iron (Fig. 5). We again find two types of adsorption: a fast and a slow adsorption. At 20° the fast stage accounts for 1.3×10^{15} O_2 molecules per cm^2 of true surface area. As Fig. 5 shows, at 35° the fast chemisorption stage causes an increase in work function of 0.1 V. When the temperature of oxygen absorption is raised to 45° and 100°, the work function decreases by 0.02 and 0.35 V respectively as compared with that of reduced nickel. At still higher temperatures (150°), an increase in work function is observed[24] with respect to the above value.

However, there have been several reports[14,36-40] of an increase in work function following oxygen chemisorption at 20° on thin films of nickel and iron prepared by evaporation in a vacuum. This disagreement is probably due, as was suggested above, to inadequate purity of the films and to their structural peculiarities.

It should be noted that the two forms of chemisorbed oxygen affect the electrochemical properties of iron in different ways. The fast stage of oxygen chemisorption has been shown, by a vacuum-electrochemical method, to increase the rate of anodic oxidation of iron, whereas the slow stage lowers the rate of the anodic process. The absorption of 4×10^{15} O_2 molecules per cm^2 produces complete passivation of this process[33,34,41]. Near the steady-state potential small amounts of O_2 (2×10^{15} molecules cm^2) chemisorbed on the surface from the gas phase cause an increase in capacitance associated with increased electrochemical adsorption[42].

Comparison of data on the influence of chemisorbed oxygen on the work function[16-18] with data on the electrochemical behaviour of iron[33,34,41] shows that the activation of the iron electrode results from absorption of oxygen under conditions leading to a decrease in work function, whereas passivation occurs when the oxygen chemisorption is accompanied by an increase in work function.

The contact p.d. method has also been used to study the mechanism of gas-phase corrosion of iron in a moist atmosphere[17].

As stated above, oxygen chemisorption at 20° lowers the work function by 0.2 V. After exposure to H_2O vapour, the work function drops by a further 0.3 V. However, there is no change of $\Delta\varphi$ after complete desorption of the water vapour, whilst the iron acquires the ability to adsorb additional amounts of oxygen. This activation of the iron towards interaction with oxygen can be repeated a number of times. As Fig. 6 shows, oxygen adsorption in amounts of 2.5×10^{15} O_2 molecules per cm^2 causes a drop of about 3 orders of magnitude in the rate of chemisorption of oxygen (curve *1*). After exposure of iron covered with an oxide film of limiting thickness to water vapour, the rate of absorption of O_2 increases again to its initial value. However, after further absorption of a small amount of oxygen the reaction rate decreases sharply, but it can be increased by repeated exposure to water vapour (curves *2*, *3*, *4*, and *5* of Fig. 6). The values of contact p.d. obtained for iron in the presence of oxygen and water vapour and

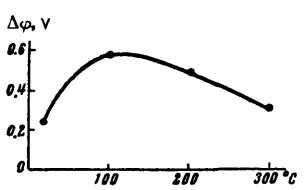


Fig. 4. Effect of temperature on the contact p.d. of iron covered with 2×10^{15} O_2 molecules cm^{-2}.

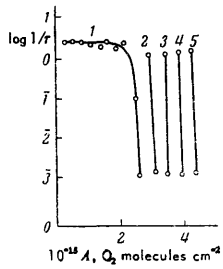


Fig. 6. Effect of water vapour on the kinetics of oxygen chemisorption by iron.

after degassing are summarised in Fig. 7. From adsorption measurements in conjunction with data on the influence of water vapour on the work function, we may conclude that the adsorption of H_2O vapour facilitates migration of metal atoms. Under these conditions, an electrical double layer with its positive pole directed outwards is formed on the metal surface, as evidenced by the decrease in work function.

We shall now consider the effect of halogens on the work function of iron.

Chemisorption of the most electronegative gas, fluorine[28], produces a most striking decrease in work function. Fig. 8*a* shows the change in surface potential of iron after exposure to fluorine. The chemisorption of fluorine was studied at a pressure of 6×10^{-2} mmHg. The results indicate that the largest decrease in work function caused by the chemisorption of fluorine on iron occurs at room temperature and amounts to 0.6–0.7 V. This value is unaffected by removal of the fluorine from the gas phase. When the iron with chemisorbed fluorine is heated in a vacuum to 100°, a slight increase in work function is observed between 20° and 100°. Further increase in temperature to 300° has practically no effect on the work function. Under these conditions, φ is lower than the value for clean iron by 0.4 V.

The change in surface potential of iron on chemisorption of chlorine was investigated[27] in the pressure range 4×10^{-4}– 6×10^{-1} mmHg. The results are reproduced in Figs. 8*b* and 8*c*. At all the pressures examined, chlorine chemisorption at 20° raises $\Delta\varphi$ from 0.1 to 0.27 V. As

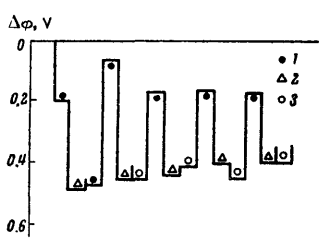


Fig. 7. Effect of oxygen, water vapour, and degassing on the contact p.d. of iron: 1) oxygen; 2) water; 3) vacuum.

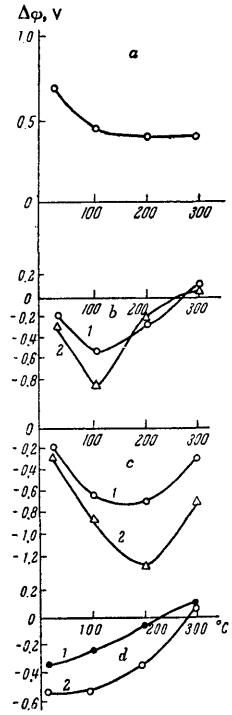


Fig. 8. Effect of halogens on the contact p.d: *a*) iron with chemisorbed fluorine heated *in vacuo* ($p_{F_2} = 6 \times 10^{-2}$ mmHg); *b*) iron with chemisorbed chlorine heated *in vacuo* [1) $p_{Cl_2} = 5 \times 10^{-2}$ mmHg; 2) $p_{Cl_2} = 6 \times 10^{-1}$ mmHg]; *c*) iron heated in the presence of chlorine in the gas phase [1) $p_{Cl_2} = 5 \times 10^{-2}$ mmHg; 2) $p_{Cl_2} = 6 \times 10^{-1}$ mmHg]; *d*) iron with chemisorbed iodine heated *in vacuo* [1) $p_{I_2} = 1 \times 10^{-2}$ mmHg; 2) $p_{I_2} = 7 \times 10^{-2}$ mmHg].

Fig. 8*b* shows, very significant changes in surface properties take place when the iron with chemisorbed chlorine is heated in a vacuum. At 100° we observe an increase in $\Delta\varphi$ from 0.1 to 0.85 V over the range of pressures stated above. With further increase of temperature the work function decreases, and reaches a value 0.1 V lower than that for a clean iron surface after heat treatment at 300°. If chlorine is present in the gas phase, a similar temperature variation is observed (see Fig. 8*c*). The only difference between these results and those of Fig. 8*b* is that the maximum contact p.d. occurs at 200° and amounts to 1.3 V.

The experiments on the effect of chemisorbed iodine on the work function[27] were done at pressures of 0.01 and 0.07 mmHg. The results are shown in Fig. 8*d*. In contrast to the behaviour of chlorine, the greatest increase in work function is found when iodine is chemisorbed on iron at 20°, and amounts to 0.3–0.5 V for the stated pressures. The chemisorption of iodine at a pressure of 7×10^{-2} mmHg amounts to 2.7×10^{15} I_2 molecules per cm^2 of true surface area. After heating to 300°, the work function becomes smaller by 0.1–0.15 V than the work function of a clean iron surface. In contrast to the results

obtained with chlorine, the contact p.d. decreases continuously when iron with chemisorbed iodine is heated in a vacuum.

As we have already remarked, the adsorption of gases with a high electron affinity (such as oxygen and the halogens) on a metal should be accompanied by an increase in work function, according to generally accepted principles. The results on oxygen chemisorption reported here indicate that the work function can either increase or decrease, depending on the adsorption conditions (temperature and amount of chemisorbed gas). Comparison of the results for the effect of oxygen and of the halogens at 20°, shows that the higher the electronegativity of the adsorbate the lower is the work function. The relationship between $\Delta\varphi$ and x (the Pauling electronegativity) is shown by curve *1* of Fig. 9. Curve *2* of the same figure shows the variation of contact p. d. with the ionic radius of the adsorbates used in this work. These results show that the amount of positive charge on the surface increases with decreasing ionic radius of the adsorbate.

According to the view previously developed by us [16-18,24,28] and now adopted by others [43-45], the decrease in electronic work function following adsorption of an electronegative gas is due to penetration of the adsorbate below the uppermost layer of metal atoms, or to migration of the latter to the surface of the adsorption layer. In the first case the size of the adsorbed ion plays the major role in determining its penetration between the surface atoms of the metal. The experiments which we have described show that adsorption at 20° of fluorine (the gas with the smallest ionic radius) produces the greatest decrease in work function. The results also indicate that the temperature at which the greatest positive shift in potential is observed is lower, the smaller the ion of the adsorbate considered. The observed changes in contact p.d. with temperature can be explained by the following argument. The positive shift of the potential of iron and nickel is caused by penetration of the adsorbate to a certain depth. Due to the difference in ionic radius, our adsorbates achieve this depth of penetration at different temperatures (at 20° for fluorine, at 100° for oxygen, upwards of 300° for chlorine and iodine). The potential of the surface become less positive as the oxygen penetrates deeper into the metal. The penetration of chemisorbed oxygen into the bulk of the metal is confirmed also by our results for platinum [25], reported below.

When penetration of the electronegative adsorbates into iron or other metals cannot take place, as in the case of chlorine or iodine at 20°, the surface becomes negatively charged. In the chemisorption of chlorine on iron, increase of temperature from 20° to 100° causes a further increase in work function, probably due to a change in the nature of the chlorine–iron bond. At temperatures above 100° the halogen can evaporate from the surface, with loss of negative charge.

Anderson [43] studied the kinetics and the mechanism of chlorine adsorption on deposited nickel films at pressures between 5×10^{-6} and 5×10^{-3} mmHg and at temperatures of 20° and -122°. Under these conditions, chlorine adsorption is very fast up to monolayer coverage. At low coverages ($\theta < 0.1$) the contact potential acquires a positive value of 0.2 V. The observed decrease in work function is attributed by the author to penetration of the chemisorbed chlorine below the surface layer of metal. At high coverages the contact potential becomes negative, with a maximum value of -1.6 V. When the nickel film covered with chemisorbed chlorine is heated to 300°, the work function decreases, in complete agreement with the results of our own work [27] reported above.

Oxygen has a different effect on the work function of platinum [25]. At room temperature and at low pressure the adsorption of oxygen on platinum is negligible and has practically no effect on the contact potential difference. Between 200° and 800° platinum can absorb significant amounts of oxygen, corresponding to 600 monolayers at 800°.

When platinum absorbs oxygen in amount of 15×10^{15}–40×10^{15} molecules cm^{-2} at 200° there is a small increase (0.2 V) of work function, which disappears if the electrode is kept for 12 h in a vacuum. The work function of the platinum is now practically the same as that of the clean metal. This can be explained by postulating that oxygen pentrates into the bulk of the platinum. The same amount of oxygen (40×10^{15} molecules cm^{-2}) has no effect at all on the work function when chemisorption occurs at 400°. This is evidently because the oxygen reaches the interior of the platinum so rapidly that $\Delta\varphi$ is not measurable.

However, as the amount of oxygen absorbed at 400° increases, the layers of platinum adjacent to the surface become saturated and the penetration of oxygen into the interior of the platinum is retarded. A larger amount of oxygen (100×10^{15}–200×10^{15} O_2 molecules cm^{-2}) causes the work function to increase by 1.5 V. However, the contact potential difference decreases with time, and after 12 h the work function becomes equal to that of clean platinum, due, as before, to the penetration of the oxygen into the deeper layers of platinum (Fig. 10). Oxygen absorbed by platinum at 800° behaves quite differently. The results

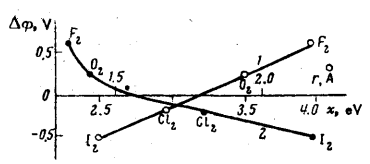


Fig. 9. Variation of the work function of iron with electronegativity x (curve 1) and ionic radius r (curve 2) of the adsorbate.

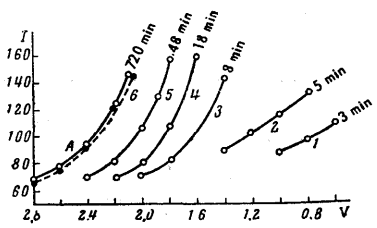


Fig. 10. Current–voltage characteristics. *A*) platinum; 1)–6) platinum covered with 125×10^{15} O_2 molecules cm^{-2}, measured 3–720 min after completion of chemisorption.

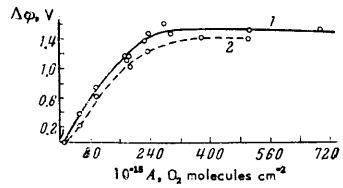


Fig. 11. Variation of contact p.d. with amount of oxygen absorbed by platinum at 800°: 1) immediately after adsorption; 2) after 12 h.

of one series of experiments are shown in Fig. 11. Increasing the amount of chemisorbed oxygen raises the work function, which remains practically constant with time and reaches 1.5 V when the extent of absorption is 233×10^{15} O_2 molecules cm^{-2}. Further oxygen chemisorption has practically no effect on the work function. The results suggest that a relatively small proportion of the chemisorbed oxygen is firmly held at the metal surface, whereas the bulk of the oxygen penetrates into the bulk of the platinum.

These conclusions are satisfactorily confirmed by measurements of the charging curve of a platinum electrode treated with oxygen at 200–800°. Cathodic polarisation can remove only a small proportion of the oxygen, equivalent to approximately one monolayer, from the platinum surface. If the cathodic polarisation is applied again after some time, it is possible to remove an additional quantity of oxygen, originally dissolved in the metal, which has now diffused to the surface of the platinum[46].

The diffusion of large volumes of oxygen into silver at elevated temperatures was demonstrated by the work of Temkin and Kul'kova[47].

It follows from the results discussed here that with a number of metals the chemisorption of gases having a high electron affinity can be accompanied by migration of the adsorbate below the surface layer of metal atoms, which causes a positive charge to appear on the metal surface. The ionic radius of the adsorbate plays an essential part in this process. The resulting decrease in work function is responsible for the activation of the electrochemical dissolution processes of metals such as iron. Chemisorption leading to an increased work function causes passivation of iron. When oxygen can penetrate into the metal to an appreciable depth, the influence of absorbed oxygen on the surface properties of the metal is relatively small.

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