Passivity of Metals and Surface Compounds

By *L. Lepin*

Almost 150 years have elapsed since the indifference of iron with respect to silver solution in nitric acid was discovered by Keir [1], and it is about 100 years since the time when subsequently to the work of Hershel [2], Wetzlar [3], Fechner [4], Daniel [5] and especially Schoenbein [6] and Faraday [7], a definite start was made in respect of an assidious and systematic study of one of the most striking phenomena in the province of metal chemistry — the phenomenon of passivity, as it was called by Schoenbein. During these 100 years, owing to the works of numerous investigators a huge experimental material has been accumulated relating to the properties and behaviour of passivated metals as well as to the conditions under which this passivity appears or vanishes. The passivating agents (such as oxidizing agents, electric current, in case the metal is taken as an anode), the effect of the activators (temperature, reducing agents, additions of some electrolytes, cathode polarisation) as well as electrochemical potentials, electrical capacity, reflecting power, photoelectric effect, X-ray photographs, electron diffraction patterns etc. — all this has already to a great extent been and still continues to be studied up to the present time. We thus have by now a rather complete picture of how

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[1] J. Keir, Phil. Trans., **80**, 359 (1790).
[2] J. Hershel, Ann. Chim. Physique, **87**, (1833).
[3] Wetzlar, Schweigg, J. Chem. u. Physik, **49**, 470 (1827).
[4] Fechner, Schweigg, J. Chem. u. Physik, **61**, 129, 151 (1828).
[5] Daniel, Phil. Trans., **114**, (1836).
[6] C. F. Schoenbein, Phil. Mag., (3) **9**, 53, 259 (1836); (3) **10**, 133, 267, 425 (1837); see also G. W. A. Kahlbaum, Monographien aus der Geschichte der Chemie IV. C. F. Schoenbein (1900).
[7] M. Faraday, Phil. Mag., (3) **9**, 53, 122 (1836); (3) **10**, 175 (1837); M. Faraday, Experimental Researches, 8th series, **2**, 237, 947 — 996.

it is possible to render this or other metal passive and what the characteristics of passivity are; for all that, up to the very present moment no uniform standpoint as regards the mechanism of the phenomenon in question has yet been established. The first theory of passivity of metals was advanced by Faraday, this being the immediate result of his attention being drawn to the unusual state of iron in nitric acid by Schoenbein (most of the experiments of the latter as well as of the predecessors were verified by Faraday). In fact, Faraday's theory is the first and virtually the only attempt to approach the solution of the problem in hand from the viewpoint of the fundamental laws of chemistry and electrochemistry. Describing the condition of passive iron Faraday says:

„My strong impression is that the surface of iron is oxidised or the superficial particles of the metal are in such relation to the oxygen of the electrolyte, as to be equivalent to oxidation; and that having thus their affinity for oxygen satisfied and not being dissolved by the acid under circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte and therefore not those successive chemical actions by which the electrical current (which is definite in its productions as well as in its action) can be considered" [8].

And futher:

„Why the superficial film of oxide, which I suppose to be formed, when iron is brought into peculiar state by voltaic association, or occasionally by immersion alone into nitric acid, is, I presume, dependent upon the peculiarities of the oxide" [8].

„The state seems to me to be one of a very delicate equilibrium of forces, though of course that condition of things which can produce it can also retain it and this notion seems to be confirmed by the intermitting action originally mentioned by Hershell" [9].

All these conceptions of Faraday are based upon the fundamental idea: „Voltaic electricity is due to chemical action and not to contact „[8] — an idea that ought to have served as a clue to all subsequent electrochemical research work but which, nevertheless, has often, if not altogether, been completely left out of account.

[8] M. Faraday, Phil. Mag., (3), **9**, 53 (1836).
[9] M. Faraday, Phil. Mag., (3), **10**, 175 (1837).

The second thesis of Faraday's theories consists, as will be readily seen from the above quotation, in the statement of the fact that the oxide formed on the surface of the passive metal is in a quite peculiar condition subject to an extremely subtle state of equilibrium.

The theory set forth by Faraday was not, as is well known, universally recognized as the leading theory in the study of the passivity of metals and various allied phenomena taking place on electrodes in course of electrolysis; and it thus failed to receive any further development. The first who was to raise any objection to Faraday's standpoint was Schoenbein. And in the sequel, throughout the history of the study of the problem, a strife may be observed to have been going on between Faraday's theory of an oxide film and a number of other theories advanced by various investigators in order to explain such facts as at first glance seemed to be in sharp contradiction with Faraday's conceptions.

In this connection we might recall the idea of Hittorf [10] who, while denying the existence of oxidation in the case in hand, believed that passive metals are in a state of tension (*Zwangszustand*). Le Blanc [11] set up a kinetic theory according to which the passivity of metals has its roots in the slow rate of reactions in a solution adjacent to the electrode (chiefly the hydration of ions). A number of investigators [12] accounted for passivity by the presence of a film of adsorbed oxygen which partly alloys with metal (the so-called *Sauerstoffbeladungstheorie* which found quite a number of adherents in its days). We may next mention the crystallisation theory of Stranski [13], the adsorption theory of Benneth and Burnham [14], and many other theories that sought for the cause of the passivity either in the appearance of certain modifications

[10] W. Hittorf, Z. physik. Chem., **34**, 385 (1900).

[11] M. Le Blanc, Z. Elektrochem., **6**, 472 (1900); Chem. News, **109**, 63 (1914).

[12] F. Fredenhagen, Z. physik. Chem., **43**, 1 (1903); **63**, 1 (1908); Z. Elektrochem., **11**, 857 (1905); M. Muthmann a. F. Frauenberger, Z. Elektrochem., **10**, 929 (1904); refer. Sackur, E. P. Shoch, Trans. Am. Elektrochem. Soc., **14**, 99 (1908); E. P. Shoch a. C. P. Randolf, J. Phys. Chem., **14**, 719 (1910); F. Flade, Z. physik. Chem., **76**, 557 (1911). See also F. Foerster, Z. Elektrochem., **17**, 888 (1911); **22**, 96 (1916).

[13] I. N. Stranski u. Z. C. Mutaftschiew, Z. Elektrochem., **35**, 393 (1929).

[14] C. W. Benneth a. W. S. Burnham, Z. Elektrochem., **22**, 377 (1916).

in metal, as for instance was the case with the allotropic theory of Smits [15], or in the alteration of metal itself, as was the case with Hittorf's conception; such were likewise the valency theory (*Wertigkeitstheorie*) of Krüger-Finkelstein [16] and that of W. J. Müller now modified by its inventor into what he calls the theory of "chemical passivation"; this latter theory together with that of the protective film which may not necessarily consist of oxides (*Bedeckungsschichttheorie*) claims to give an exhaustive (quantitative) theory of passivity [17].

All these theories seem, in point of fact, to be concerned but with a single aspect of the phenomenon, and we would say that they leave a series of attendant facts unaccounted for or else set constructions for their explanation, which cannot be qualified otherwise than entirely artificial. The kinetic theory as well as the „*Sauerstoffbeladungstheorie*", while readily accounting for the cause of the activating effect of temperature, are unable to explain the activating influence of halogen ions. At the same time the film theory accounts for that influence by the peptizing effect on these ions and maintains that the film covering the metal and passivating it has a colloidal nature and is pierced by a number of pores which are not equally accessible to different ions.

A careful examination of all the theories so far advanced as well as of all the available experimental material connected with the polarisation of electrodes in electrolysis, the passivating or activating action of electrolytes, as well as the results of experimental research on the characteristic phenomena which take place on the surface of such solids as active ash-free sugar charcoal during the adsorption of electrolytes [18, 19] lead us to the following conclu-

[15] A. Smits, Z. physik. Chem., **88**, 743 (1914); A. Smits u. A. H. W. Aten, Z. physik. Chem., **90**, 723 (1915); **92**, 1 (1918); see also A. Smits, Z. Elektrochem., **36**, 20 (1930).

[16] A. Finkelstein, Z. physik. Chem., **39**, 91 (1902).

[17] W. J. Müller, Z. physik. Chem., **48**, 577 (1904); Z. Elektrochem., **10**, 518 (1904); **11**, 823 (1905); **15**, 696 (1909); **30**, 401 (1924); **33**, 401 (1927); **35**, 93 (1929); **36**, 679 (1930); **41**, 641 (1935). See also Monatsh. 48 — 70 (1927 — 1937.)

[18] A. Frumkin u. A. Donde, Ber. Dtsch. chem. Ges., **20**, 1816 (1927); B. Bruns u. A. Frumkin, Z. physik. Chem., (A) **141**, 141 (1929); R. Burstein u. A. Frumkin, Z. physik. Chem., (A) **14**', 158, 219 (1929).

[19] N. Shilov, Koll. Z., **52**, 107 (1930); N. Shilov u. K. Tschmutov, Z. physik. Chem. (A) **148**, 233 (1930); N. Shilov, E. Schatunow-

sions: if Faraday's views expounded a century ago be given a more precise interpretation than heretofore, it seems possible to construct a most simple and rational chemical theory of passivity which would permit to give a satisfactory explanation to all the processes taking place on the surface of metals.

This theory can be reduced to the following statements:

1. Faraday's oxide films are not any ordinary familiar compounds of metal and oxygen, as this used to be supposed by the first critics of Faraday's theory, and is now asserted, for instance, by those investigators who connect passivity with oxidation or else try to isolate the protective film of oxide by removing it from the surface of the metal [20]. The "peculiar condition" referred to by Faraday offers in fact a rather unusual condition entirely distinct from the ordinary condition when a substance can be isolated as a wholly definite volume phase.

2. Faraday's oxide film which is responsible for passivity is not a new phase [21] formed in result of oxidation, but is what may be termed a surface compound. This surface compound differs from the usual „volume" compounds in that it clings tenaciously to the whole groundwork, to the whole crystal lattice of the solid (metal or other element) and, therefore, cannot exist in the form of a new phase entirely separate from the parent metal.

3. Being thus indeterminate both from the point of view of the phase rule and from the standpoint of stoichiometry, these surface compounds are, however, endowed with all the properties of true chemical compounds. We may expect to discover here and as a matter of fact actually do discover that these surface compounds, just like volume compounds, may correspond to different degrees of oxidation, *i. e.*, they may be characterised by different numbers of atoms of oxygen bound up with the surface atoms of the metal.

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skaja u. K. Tschmutov, Z. physik. Chem., (A) **149**, 211, **150**, 31 (1930); L. Lepin, Sow. Phys., **4**, 282 (1933); L. Lepin u. G. Strachowa, Z. physik. Chem.. (A) **173**, 129 (1935); **176**, 303 (1936).

[20] U. R. Evans, J. Chem. Soc., 1020 (1927); 92 (1929); U. R. Evans a. J. Stockdale, ibid. 2651 (1929). See also L. Tronstad u. T. Höverstadt, Z. physik. Chem., (A) **170**, 172 (1934).

[21] A similar opinion has been outlined by G. Tamman (Z. anorg. Chem., **107**, 104, 1919) but failed to receive any further development.

At the same time the hydrates of these surface compounds — surface hydroxides — may be distinguished by different power of dissociation, *i. e.*, they may have a basic or acid nature. This idea was first expressed by N. A. Shilov [19] with regard to the surface of active charcoal.

Let us now give an example throwing some light on what has been stated above: passive iron in contradistinction to ordinary active iron does not react with oxygenous acids or their salts. This may be accounted for by the fact that the surface oxide which covers passive iron is an oxide of one of the highest valencies of iron possessing the properties of anhydride [22]: it does not react with acids but can react and, in fact, does react with alkalies forming "surface salts" — a process which occurs during anodic passivation in alkali solution. Likewise it ought to behave and indeed does behave as an oxidizing agent with different halogen hydroacids and their salts as well as with the salts of ferrous oxide in the presence of which the surface oxide must pass into a lower degree of oxidation; at the same time with sufficient strength (reducing potential) as well as with sufficient concentration of the reducing agent the surface oxide will lay bare the free surface of the metal. It is by this fact and none other that the activating effect of halogen ions upon passive iron may be explained.

Further, it is well known that the behaviour of iron or some other metal as anode in passivating solutions such as those of oxygeneous acids or their salts is characterised by a quite peculiar S-shaped form of the polarisation curve (the curve: potential — current density). In other words, given a definite current density, the potential begins to rise sharply with the current density and soon attains the limiting values which are characteristic for the potential of the oxygen liberated on noble metals. This curve may be interpreted in the following way: on the lower branch of the curve we have the ordinary "active" metal, *i. e.*, a metal which under experimental conditions is capable of giving but low degrees of oxidation, but in reacting with acids forms volume compounds passing into solution. As the current density increases, the oxygen begins

[22] W. J. Müller (Z. Elektrochem., **10**, 518, 1904) was quite right when he expressed his firm conviction to the effect that valency takes a certain part in passivity.

to be liberated at the anode and immediately starts reacting with the surface of the metal, producing oxides of high valencies which gradually cover all the active spots of the surface. With the formation of such surface oxides the metal no longer passes into solution and the potential reaches the limiting values under given conditions.

4. Let us now attempt to make a step further. In giving his characteristic of the peculiar voltaic condition of iron Faraday points out that "the iron wire rendered inactive either by occasion with the oxidized wire or in any other way is also as platinum to the platinum and produces no current". Or "the oxidised wire is exactly as another piece of platinum would be". We believe that we are likewise fully entitled to say that the noble metal platinum behaves in exactly the same manner as passive iron or as any other passive metal. In other words, platinum as well as any other noble metal, is "noble" because already under ordinary conditions it bears "surface compounds" with oxygen on its surface.

These surface oxides belong to one of the highest valencies of the metal and possess an acid nature. All the so-called noble metals are not virtually noble in the least, but are fully capable of forming a most firm bond between the surface atoms and oxygen (in an atmosphere of oxygen) or other gaseous metalloids under other conditions.

5. We necessarily come to the conclusion that the elements of Mendeleeff's periodic system and particularly the metals will, depending upon the conditions under which they are placed as well as upon their position in the system, form either volume or surface compounds. In any of the periods of Mendeleeff's system we can trace an ever-increasing power to form surface compounds, especially so, when the middle of the period is approached. This is particularly manifested in the triads of the 8th group in the long periods. It may be said that metals which start the periods, metals of large atomic volume with a weak crystal lattice providing for their greater volatility, yield principally volume compounds. Yet the denser the space lattice of the metal is and the greater its energy becomes, *i. e.*, the less the atomic radius of the metal and the less its volatility — the lower is the ability of the metal to take part in ordinary volume reactions and the easier will it be for

that metal to participate in surface chemical action. If we cast a glance at the periodic system, we shall readily find the groups of elements which ought to give surface compounds the more easily. These are the elements which occupy their places in the middle of the long periods, *i. e.*, the metals of great density and high melting point, with a complex electronic structure of their atom periphery for which reason they may be chemically charaterized by a variable valency, namely:

V, Cr, Mn, Fe, Co, Ni, Cu;
Nb, Mo, Ma, Ru, Rh, Pd, Ag;
Ta, W, Re, Os, Ir, Pt, Au.

Let us now try and gain some insight from the above viewpoint into some of the chemical actions characteristic of the noble metals: Pt or Au do not react with HNO_3, and only very slowly with HCl in the presence of oxygen. *Aqua regia* is used to dissolve them. But in this process not only does the oxidation of the metal play part, as is usually considered to be the case, but also the reduction. Here, just as in the case of the activation of passive metals by the ions of halogens, the part of the reducing agent is taken by the Cl-ions. These ions reduce that high-valent surface oxide by which Pt or Au are liable to be covered, and owing to the simultaneous action of the oxidizing agent this surface oxide is being continually renewed on the metal. One may interpret in the same sense the experiments on the dissolution of the Pt-anode which occurs owing to alternating current being superimposed upon continuous current, the part of the reducing agent being in this case taken by the cathodic component of the alternating current (as was first observer by Margules and afterwards proved by Ruer [23]).

The soundness of the surface oxides must evidently be associated with the closeness of packing of the crystal lattice of the solid. And indeed, metals with most closely packed lattice and the highest melting poing like Os, Ir or Rh are as is well known immnne from the action of *aqua regia*: in order to convert them

[23] R. Ruer, Z. physik. Chem., **44**, 81 (1903); Z. Elektrochem., **9**, 235 (1903).

into a „soluble" state it is necessary to expose them to the simultaneous action of both chlorine and molten chlorides of alkali metals which are, as it would seem, needed not only for the formation of complex compounds here occurring, but also in order to play the part of reducing agents for the surface oxides of these metals whose affinity for oxygen is very great.

6. By varying the external conditions affecting the metal it is apparently possible to realise the transformation of surface compounds into volume ones. Thus by subjecting iron to anodic passivation in concentrated solutions of alkalies or their melts, we obtain ferrates (this method for obtaining ferrates belongs to Poggendorf and was later developed by Haber and Pick [24]). Likewise, chromium, while retaining the high potential of a noble metal in the course of anodic passivation, passes into solution in the form of chromic acid. Such a transformation of surface compounds into volume ones involves, as a matter of fact, the expenditure of a certain amount of energy needed for the breaking up of the bond which connects the surface atoms of the metal with the crystal.

Hittorf spoke about the necessity of this excess energy being spent when he compared the behaviour of passive iron and chromium. In the course of anodic passivation under uniform condition iron yields only surface compound, whereas volume compound is also formed in the case of chromium; in other words, in this case the input of energy is sufficient to tear the surface atoms away from the lattice.

The chemistry of surface compounds is obviously not confined to surface oxides. There cannot be the slightest doubt that other gaseous metalloids are equally capable of producing surface compounds on metals. This formation of new surface compounds is determined by the ratio of the energy of the formation of the given compound to the energy of the crystal lattice of the metal. It is also evident that such a phenomenon as cathodic overvoltage in course of hydrogen liberation is brought about on the one hand by the same surface oxides and, on the other hand, by the formation of surface hydrides. However, in the case of hydrogen, owing to the

[24] F. Haber u. W. Pick, Z. Elektrochem., **7**, 215, 713 (1900).

small volume of its atom, the phenomenon in question will certainly be complicated by the penetration of hydrogen into the metal, accompanied by the formation of quasi-volume phases inside the crystal lattice.

In summing up we feel that we necessarily come to the following conclusion: if Faraday's theory of passivity first advanced a hundred years ago would have been further developed along the right lines, we should now be much more enlightened on everything that takes place on the surface of solids, especially when we use them as electrodes. Furthermore, modern chemistry would now number among the objects of its investigation as many surface compounds as it already does among the volume ones.

Summary

Faraday's oxide film theory of passivity of metals is enlarged and it is shown that the phenomenon of passivity as well as the indifference of noble metals are due to the formation of surface compounds, namely surface oxides of high valency, which render the metals inactive towards the oxidising agents. The ability to form surface compounds depends upon the position of metals in Mendeleeff's periodic system. The denser the space lattice of the metal is, *i. e.*, the less the atomic radius of the metal, the less able is it to take part in ordinary volume reactions and the easier will it be for it to participate in surface chemical actions.

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