THE PHENOMENA OF PASSIVITY.

(Translated from the German.)

A Paper by **Professor Max Le Blanc** (Leipzig) on "The Phenomena of Passivity" was read in abstract by Dr. T. Martin Lowry.

In response to the kind invitation of the Faraday Society, I take the opportunity of giving a brief survey of the phenomena of passivity, and I shall attempt to present them viewed from a uniform standpoint.

The first observations relating thereto are more remote than one usually supposes: even at the end of the eighteenth century, at the time of the discovery of galvanism, James Keir,* following on still earlier experiments by Bergman, remarked that when he poured an unsaturated solution of silver in pure colourless nitric acid upon a piece of pure iron wire, a reaction did indeed take place at first, with the separation of metallic silver; but the action of the iron upon the liquid soon ceased and the silver redissolved. Then for several weeks the iron lay at the bottom of the vessel, apparently unchanged and bright.

It is interesting to note that Keir became aware of the instability of this peculiar condition: it was lost by scratching the piece of iron, as also by touching it with a new piece.

The phenomenon was not then further investigated until 1827, when it was rediscovered by Wetzlar,† who drew attention to electrochemical relations. Fechner‡ then made electrical measurements, which showed that by forming an element of iron-silver in a silver solution the iron remained electropositive so long as it possessed the power of dissolving spontaneously and reacting chemically. As soon as this power disappeared it became electronegative.

At the end of the thirties the investigation was continued by Schönbein,§ who published a mass of new details; especially he showed that the inactive condition of iron can be brought about by making it in a suitable manner the anode in aqueous, even dilute solutions of different oxyacids. He introduced the expression "passive," which has ever since been retained.

At this time it was known that other metals than iron could also assume this peculiar property of passivity.

Attempts to account for the phenomena of passivity have naturally been made. The discoverer himself, Keir, had thought about the matter, as can be seen from the closing words of his paper: "The explanation of these phenomena will be attempted in the subsequent paper." This promise, however, he did not fulfil.

Fechner thought of the formation of a protective coat, but the observation of the iron convinced him that it was so bright that oxidation seemed quite out of the question.

* *Phil. Trans.*, **80**, 374, 1790.

† *Schweiggers Journ. f. Chemie u. Physik*, **49**, 470; **50**, 88 and 129, 1827.

‡ *Ibid.*, **53**, 141, 1828.

§ *Poggend. Ann.*, **37**, 390 and 590, 1836.

Faraday held a different opinion, and expressed himself thus*: "My strong impression is that the surface of the iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the 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 electric current (which is definite in its production as well as in its action) can be continued."

This oxide theory, with numerous modifications, has been adopted up to quite recent times by a large number of investigators without any surer proof of its correctness having been brought. On the other hand, certain facts have become known which either cannot or only with difficulty can be brought into line with the theory of an oxide layer forming a protection for the electrode. Most important is the discovery of Müller and Königsberger,† according to whom the reflecting power of iron in alkaline solutions is identical in the active and in the passive state; they proved, besides, that a layer of lead peroxide of approximately molecular thickness ($0.8 \mu\mu$) deposited upon a platinum mirror greatly diminished the reflecting power of the mirror, and the optical constants of the known iron oxides and hydroxides differ only very slightly from those of lead peroxide; hence these workers both come to the conclusion that the passivity of iron is not occasioned by a coating of oxide.

Krüger‡ has recently come to the same conclusion by measuring the reflecting powers of passive and active iron for ultra-red rays.

One may object that the hypothetical oxide may have other properties than the known oxides, but one would have to confess that such an *ad hoc* supposition would be arbitrary and improbable. The same can be said of the supposition that the layer is so extremely thin that it only just covers the surface, but cannot be detected by even the most sensitive optical method. It is indeed not comprehensible on what grounds the protective layer should be formed in just such small dimensions, for in those cases in which no one doubts the formation of oxide—as, for example, in the case of the anode treatment of lead electrodes in sulphuric acid or in sodium chromate solution—the conducting metallic oxide which covers the surface after a short time becomes easily visible to the naked eye.

Such firmly adherent anodic layers, which protect the underlying metal, are always formed in electrolysis with simultaneous evolution of oxygen if the electrolyte consists simply of a salt, whose anions form with the anode metal a compound soluble with difficulty.§ Should, however, excess of another salt be added, whose anions form an easily soluble salt with the anode metal—*e.g.*, sodium chlorate in the case of lead anodes in sodium chromate solution—there is neither evolution of oxygen nor the deposition of any firmly adhering precipitate on the anode, but a precipitate is quantitatively produced, which falls away from the electrode, which remains bare. This process has been applied for the technical production of substances soluble with difficulty, such as white lead, and it is based upon the fact that in consequence of the simultaneous action of the excess of chlorate ions nearest the

* *Phil. Mag.*, **9**, 61, 1836.

† *Z. für Elektroch.*, **13**, 659, 1907; **15**, 742, 1909.

‡ *Vortrag auf der Hauptversg. der deutschen Bunsen Ges. zu Breslau*, 1913.

§ Le Blanc and Bindschedler, Isenburg, Just, *Z. f. Elektroch.*, **8**, 255, 1902; **9**, 275 and 547, 1903.

electrode a layer of liquid free from chromate ions forms soon after the commencement of the electrolysis. This layer prevents the formation of precipitate in the immediate vicinity of the electrode, and consequently also prevents any adhesion thereto.

How do *passive* electrodes behave in such cases? Nickel is passive under anodic treatment in pure potassium sulphate solution and oxygen is evolved; in pure sodium chloride solution it easily dissolves. On adding sodium chloride to the potassium sulphate solution, solution of the nickel still takes place with a moderate current density, whilst the evolution of oxygen ceases, but no detachable precipitate becomes visible. So that this observation is also unfavourable to the supposition that all cases of passivity are due to the formation of a good conducting protective layer on the electrode.

Furthermore, the strong influence of rise in temperature in restoring the activity of the metal concords ill with the oxide theory, and also the remarkable instability of this layer must excite wonder, since it finds expression in the spontaneous return of the metal to a more or less active state when the means of bringing about the passive condition are withdrawn.

This last point has already been raised by Schönbein (*loc. cit.*) as an argument against the oxide theory of Faraday. The particular passage reads thus: "A further important circumstance, to which attention must be drawn, is the fact that the iron wire, which dips in the dilute acid and remains indifferent to it, becomes attacked as soon as the electric current no longer passes through it. For instance, by leaving the wire dipping in the acid and opening the circuit in some way, there appear instantly yellowish-brown streaks shooting downwards, *i.e.*, ferric nitrate. . . . It is also clear that if the passivity of the positive iron wire be due to a film of oxide upon it, then the same wire, when removed from the circuit and placed in ordinary nitric acid, should remain passive: but this is not the case."

Thus from the various facts quoted, which can also be amplified, it is evident that the hypothesis of an impervious layer, which covers the surface of the metal, thereby protecting it from contact with the electrolyte, is open to the most serious objection.

We shall therefore attempt to arrive at an understanding of the phenomena of passivity on other grounds; this brings me to the polarization measurements for metals, immersed in their respective salt solutions, which I carried out some years ago.* Although these measurements may seem to have little to do with the problem in hand, we shall presently see that they can be brought to bear very closely upon it.

Let us take as our basis for the calculation of the potential difference at a metallic electrode Nernst's formula: $E = \frac{RT}{n_e F} \log \frac{P}{p}$ (R = gas constant; T = abs. temp.; n_e = valency of the metal; F = 96,540 coulombs, P = constant for a given metal under given conditions (the electrolytic solution pressure); p = osmotic pressure of the corresponding metal ions). Let us suppose also that the formula can be applied for any desired variable condition, so long as it be reversible; then at constant temperature polarization, and consequently a rise in potential difference, can only occur in consequence of a change in value of P or of p . If we exclude the former by using a specified metal electrode, the electrode potential can only be changed by changing p , or, since p depends upon the concentration of the solution of metallic salt, simply by changing the concentration of the solution.

From this point of view we might expect that when employing a system:

* Le Blanc, *Abhandlungen d. deutschen Bunsen Ges.*, No. 3, 1910; W. Knapp, Halle-a.-S.

metal—a not too dilute solution of a metallic salt—metal (*e.g.*, copper-cupric sulphate solution-copper), no appreciable polarization would take place in the case of a short-timed electrolysis with a moderate current density, for under such circumstances no marked change of concentration of the electrolyte at the electrodes can occur. This expectation was fulfilled in the cases of the systems: lead-lead nitrate solution-lead; and mercury-mercurous nitrate solution-mercury; in all the other cases that were tried, anodic, and at the same time cathodic, polarization occurred in spite of an ample ion concentration; especially was this the case in the systems: copper-cupric sulphate or chloride in water-copper; silver-silver nitrate solution in water or in acetonitrile-silver; iron-ferrous chloride in water-iron; nickel-nickel chloride in water-nickel. The degree of polarization was dependent on many influences; for example, on the current density, the temperature (with rise of which it decreased), and the condition of the electrodes and solution. In many cases it could be greatly increased by addition of extremely small quantities of strychnine, brucine, gelatine, etc., and, indeed, always both at the anode and the cathode; the increase amounted to several tenths of a volt.

How can these facts be explained? Let us disregard the unlikely supposition that various obstructions oppose the processes of charging and discharging. Is there, however, not the possibility that the interchange of charge may be associated with a chemical reaction of changing velocity?

If we first consider the action at the anode, it is conceivable that primarily no metal ions are formed, as generally supposed, but that the electrical process consists of a discharge of negative ions and the chemical process of an interaction between the non-electrified radical and the metal. The potential difference would, according to this view, depend upon not only the concentration of the negative ions, but upon that of the separated non-electrified radical, and consequently upon the velocity with which the latter reacts upon the metal. For the smaller this is (*ceteris paribus*), the greater must the concentration become for a given current density, until the velocity of the reaction, which by the law of mass-action also increases, has become so great that in unit time as much of the radical disappears through chemical action as is produced by the electric current.

This view is certainly justified for series of solids, such as silver-silver sulphate or chloride-silver, which according to the researches of Haber and Zawadzki* even at low temperatures show considerable polarization at the anode; nor can any serious objection be made to its application to the series of liquids quoted above, but in the latter case we are not obliged to relinquish the usual idea of the preliminary formation of metallic ions, in order to be able to assign the observed polarization to failing chemical reaction velocity; we need only adduce the probable extensive hydration of the metal ions (or their combination with the solvent). The process of hydration which occurs at the surface of the electrode, and whose velocity depends on different influences, must then follow on the formation of ions, which, when the current passes, is practically infinitely rapid. The magnitude of the potential difference is then, it should be carefully remarked, dependent only upon the concentration of the non-hydrated, free ions, and the latter again upon the velocity of hydration. In this way polarization, which changes according to circumstances, easily explains itself—also its decrease with rising temperature, since the chemical reaction velocity increases almost without exception with rising temperature.

In a similar manner the cathodic polarization, which in these experiments always accompanies that at the anode, can be explained. The free ions must,

* *Zeitschr. f. physik. Chemie*, **78**, 228, 1911.

in the state of equilibrium, according to the law of mass-action, always be present in addition to the hydrated ones, and when the current passes they are discharged. Consequently a diminution in concentration and then polarization follows, owing to the insufficiently great speed of the formation of free from hydrated ions. Indeed, the simultaneous occurrence of polarization at the anode and the kathode finds a satisfactory explanation in this hypothesis, for both result from the same reaction: $\text{ionhydrate} \rightleftharpoons \text{ion} + \text{water}$, which takes place at both electrodes in opposite directions, and any catalytic influence, such as the quoted case of the addition of strychnine, must change the velocity of the reaction in either direction in the same proportion. Indeed, as has been pointed out; a simultaneous increase of polarization was always observed at the two electrodes.

In addition to this cause, another can be considered in the case of cathodic polarization; we may expect that the discharged metallic ion frequently does not separate as solid metal, but remains at first dissolved, forming a supersaturated solution. With increasing supersaturation polarization must increase.

The absence of polarization of the mercury and lead compounds points to the fact that in these cases the chemical and physical processes concerned take place with greater velocity.

It should be expressly understood that all the foregoing experiments were carried out under such conditions that the metals dissolve without evolution of oxygen under the action of equal currents according to Faraday's law, and further that polarization is not occasioned by any ohm-resistance at the electrodes. Were this the case, polarization would *immediately* disappear on breaking the current, whereas a gradual decline was actually observed, which could easily be followed and measured; in other words, the above-mentioned systems, which before the passage of the current possessed no e.m.f. and were unable to give a current, could do so after having first passed a current and then broken it. Hence it was proved that both at the anode and at the kathode, which could be separately examined, a condition was brought about which, at the cessation of the current, had electromotive power.*

If we account for the polarization here observed by this explanation of failing reaction velocity, we can go a step further and apply the same explanation to the phenomena of passivity. With passive metals ionic hydration occurs so slowly at the anode (a certain amount of solution nearly always takes place), that the concentration of free ions, and therefore the potential difference, becomes so great in a short time that visible separation of the negative radical or of oxygen can result. Qualitatively these phenomena present nothing new in comparison with those described before; quantitatively they are only in so far remarkable as the chemical polarization has become so strong that solution of the metal practically ceases and the negative radicals (or oxygen) are separated and become visible.

From this point of view we ought henceforth to understand by passivity phenomena all such as result from chemical polarization. We have seen that passivity is not the exception but the rule, and that it is not connected with oxygen-containing anions, as was supposed, but that it takes place also with chlorides and other solvents, and especially that it can also take place at the kathode.

* The same explanation holds for the supertension which occurs at the electrodes with liberation of gas, which also has electromotive power. I mention this because recently J. W. Richards has erroneously attempted (*Trans. Faraday Soc.*, 9, 140, 1913) to characterize this supertension merely as resistance.

Briefly it may be mentioned that one may ascribe the peculiar shift in valency which occurs on dissolving many metals, *e.g.*, chromium, by altering the experimental conditions, also to the changing hydration velocity of the ions of different valency.

I have thus attempted to establish as a fact that passivity phenomena are to be traced to those of reaction velocity. The reaction velocity theory can as yet afford no special information upon the conditions under which a metal becomes active or passive. Still one cannot reasonably regard this circumstance as a defect of the theory ; it is rather due to the fact that our knowledge of the effect in chemical reaction velocities of outside factors is extraordinarily deficient. Thus another wide field is opened up for special research, and the work is being carried out with assiduity.