THE RECOVERY OF TRANSMISSIVITY IN PASSIVE IRON WIRES AS A MODEL OF RECOVERY PROCESSES IN IRRITABLE LIVING SYSTEMS.

PART II.

BY RALPH S. LILLIE.

(From the Physiological Laboratory, Clark University, Worcester.)

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Theoretical Considerations.

The consideration of why transmission is only partial during the early period after repassivation must take account of a number of factors whose precise mode of action is not clear in all cases. It is evident that the return to the passive state implies redeposition of a continuous surface layer of oxidation product; it is also evident from the behavior of the newly passivated wire that when first deposited this layer is in a different chemical and physical condition from that which it afterwards attains when complete transmissivity is reestablished. The question is what kind of change occurs in the surface layer during the period of progressive recovery; e.g., in 70 per cent HNO₃ during the first 7 or 8 minutes after the spontaneous return of passivity.

Several peculiarities are to be noted in the character of the activation wave at the successive intervals. There is an evident correlation between its speed and the distance which it travels. At first the local reaction spreads slowly and for only a short distance; at each successive trial the wave travels faster and advances farther; eventually it travels for an indefinite distance at a high speed (several hundred centimeters per second). It is also noticeable that an activation wave which comes spontaneously to rest after traveling some distance is visibly retarded through the last 2 or 3 cm. of its path (though not
evidently retarded earlier); this retardation is more readily seen at low temperatures (3°C.), and in general in slowly moving than in rapidly moving waves.

It is well known that the advance of the wave is due to local cathodic reduction at the boundary region between the active and the passive areas of the metal, the passive area being cathodal. The diagram (Fig. 1) illustrates the conditions. The active area is anodal and the adjoining passive area cathodal. The local intensity of the current passing between the solution and the passive metal at any point decreases with increase in the distance from the boundary line X, because of the increase in the electrical resistance of the circuit which includes the point under consideration. This resistance depends almost entirely upon the length and the specific electrical resistance of the column of electrolyte between the point in question and the boundary line. The local reducing action, which is a function of the local intensity of the current, thus decreases as the distance from the boundary increases, i.e. in the order A < B < C, and beyond a certain distance from the boundary (e.g. XY) it will be insufficient to

Fig. 1. Indicating the conditions of the local circuit at the boundary between the active and the passive areas; the direction of the current (positive stream) is indicated by the arrows. The active region (shaded) is anodal, the passive cathodal. See text.

1 Adrian (Adrian, E. D., J. Physiol., 1914, xlvi, 53) finds no evidence of change in the velocity of the excitation wave in the nerve as it passes along a region of decrement; but, as he himself points out, his observations do not refer to the rate of conduction immediately before the extinction of the wave. He concludes that “if the rate of conduction is ever affected by the size of the disturbance it can be only when the disturbance is so small as to be on the verge of extinction.” In the passive wire also the rate of transmission does not undergo evident retardation until immediately before extinction.

effect reduction; during transmission, therefore, we are to assume that the removal of the film by cathodic reduction is continually in progress through a certain distance in advance of the boundary. The rate of this reducing action, and the distance from the boundary through which it is effective (i.e. the length of XY) are the two chief factors determining the speed of propagation.

It seems probable that in the decrement type of transmission the removal of the passivating film by cathodic reduction in the region XY adjoining the boundary is everywhere incomplete, and that the progressive decline in the traveling power of the activation wave is thus to be explained. In the case just considered, however, in which the local reduction is assumed to be complete, with consequent exposure of a free surface of metallic or "active" iron over the entire area XY, there will inevitably be complete transmission; i.e., the activation wave, once set up, will travel through an indefinite distance, since then the area secondarily activated by the local current will have the same properties as the original active area; accordingly the current conditions at the boundary of this new active area will be the same as at the original area, and these conditions will be repeated at every new boundary as the active region extends. With exact repetition of the same reducing effect at the cathodal (i.e. passive) area adjoining each new boundary as it is formed, there is nothing to prevent transmission through an indefinite distance. In transmission with a decrement, however, it is evident that the chemical effect at each new boundary is somewhat less than before, as shown by the progressive decline in the traveling power of the activation wave. If, as the above hypothesis holds, the removal of the passivating film near the boundary is in this case only partial, this partially activated area will not reach the full anodal potential characteristic of a freely exposed iron surface; and the reducing effect at the passive area adjoining will be less than at the original active area; i.e., there will be a progressive decline in the reducing power of the local circuit as the active area advances. Eventually, when the boundary of the active region has advanced for a certain distance from the starting point, the P.D. of the local circuit will fall below the critical value (i.e. the decomposition voltage) required for appreciable reduction; the advance of the active region will then cease, and the line of cessation will be
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sharply defined. According to this hypothesis, the P.D. across the active-passive boundary decreases progressively as the activation wave passes along a region of decrement. When the rate of this decrease is gradual, there will be transmission through a relatively great distance before the wave comes to rest; when it is rapid, transmission will be correspondingly limited.

This hypothesis is also consistent with the fact that the return of transmissivity is more rapid in weak than in strong acid, its rate being approximately inversely proportional to the excess of concentration above a certain critical level (about 53 to 54 volumes per cent). Two chief factors may be distinguished in the chemical part of the passivating process, i.e. in the reaction which reforms the passivating surface layer of oxide: (1) the general oxidative action of the solution, which is the more intense the higher the concentration of HNO₃; and (2) the electrochemical oxidative action at the anodal region of the local active-passive circuit. This anodal area, i.e. the active region of the metal, is automatically subjected to the oxidizing—and hence passivating—influence resident at every anode. The difference in the rate of repassivation is an index of the energy of the local oxidizing process; in acid of 50 volumes per cent (about 7.5 N) or lower this is not sufficient to rebuild a stable surface film, hence the metal continues to dissolve in this solution; in 55 per cent acid the oxidative action is intense enough to deposit a permanent film in 5 or 6 seconds (at 20°); in 60 per cent acid the rate of deposit (i.e. of repassivation) is several times more rapid; and at higher concentrations still more rapid. The low degree of transmissivity found immediately after repassivation suggests that the passivating film when first deposited is relatively thick (or relatively dense or otherwise resistant to alteration) in comparison with what it becomes later, when the state of transmissivity without decrement is reached. This view would imply that the quantity of passivating material deposited during the reaction

\[ C - 54 = \text{constant} \]

The formula \( C - 54 = \frac{t}{t} \) expresses fairly well the relation of the total recovery time to the concentration of the acid, where \( C \) is the concentration and \( t \) the recovery time. 53 to 54 per cent is the critical concentration; and the time required for the return of complete transmissivity is about proportional to the excess of concentration above this value.
is closely proportional to the excess of concentration of the acid above a certain critical limit (of about 53 to 54 per cent). Hence in strong acid the film at its first deposition has a thickness (or a structure) such that the relative quantity removed by the cathodic reduction at the active-passive boundary when the metal is locally activated is less than in weaker acid. The decrement of transmission is hence from the first steeper in the strong acid, and a greater time is required for the removal of the surplus film material (by the solvent action of the acid) until it attains a degree of thinness permitting of rapid and complete removal under the influence of the local circuit.

The important fact from the point of view of the physiological comparison is that after the decrement stage has passed the local reaction is complete and does not admit of gradations. Transmissivity is then complete and the wire as a whole exhibits an "all or none" type of response. This stage is a permanent one, as long as the metal remains undisturbed in the acid, and apparently it corresponds to a condition of minimal thickness of film. Judging from the analogy with adsorption processes in general, it seems probable that at this stage the film is only 1 molecule in thickness. It is evident that with a film of this thickness there would be no possibility of gradation in the local action; either it would be complete or would not occur. Uniform and complete action at the different areas of the surface in a transmitting wire would thus be necessitated, with the result that the activation wave would be transmitted for an unlimited distance with a uniform velocity whose exact degree would be determined by the local rate of reduction of the film.

These considerations lead to the conclusion that the condition reached by the passivating film when complete transmissivity is regained is one in which its material is spread out in a uniform layer of 1 molecule in thickness. In this respect it corresponds in structure to films of oil or fatty acid which have spread over the surface of water to an equilibrium stage, as in Langmuir's experiments. The precise composition and structure of the film do not concern us at present;

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4 Cf. Lillie, R. S., J. Gen. Physiol., 1920–21, iii, 119, Table II; and 125, Fig. 3.
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...it is an oxidation product and is usually regarded as a higher oxide of iron.7

...The question remains why the film persists for an indefinite period with unaltered properties, even in acid of a strength lower than that required to passivate. Why should not the film undergo still further solution and eventually lose its continuity and break down? In point of fact, the passivating film is unstable except in solutions possessing considerable oxidizing power;8 its preservation thus appears to depend upon a more or less continuous process of slow oxidation; this process exercises what may be described as a regulative control over its local variations of composition or thickness. That this is the case is indicated by the general fact that passivity disappears spontaneously in pure water and in solutions of salts and other substances, except those having strong oxidizing properties. In the latter case there is evidence that local interruptions of the film (unless too extensive) are automatically repaired by local oxidative action. This may occur even in solutions whose oxidative properties are insufficiently intense to repassivate a completely activated wire. The case of nitric acid of specific gravity 1.20 or less will illustrate; in this solution an active wire continues to react until it is completely dissolved, but a passive wire remains unaltered indefinitely. I have already described how a film partially destroyed by brief immersion in 1/1,200 NaCl is restored to its original state by brief immersion in 1.20 HNO3.9 A similar restoration after partial mechanical removal of the film is seen when the passive wire, while immersed in 1.20 HNO3, is scraped locally with a piece of glass; in order to secure activation by this means several scrapes in rapid succession are as a rule required; if the interval between successive scrapes is lengthened this characteristic summation effect is less readily obtained. When a wire which is thus treated is connected through a voltmeter with another wire (e.g. of passive iron or platinum) serving as an indifferent electrode, there is seen at each scrape a slight temporary excursion of the needle.


8 For examples of this behavior cf. Lillie, R. S., Science, 1919, 1, 259, 416.

9 Lillie, R. S., Science, 1919, 1, 259.
of the instrument, the scraped wire becoming more negative, indicating the formation of an anodal area. The range of this excursion is increased by a rapid succession of scrapes, and when a critical point is overpassed a propagated activation wave is started and the whole wire is activated. The reaction thus produced is permanent in acid of specific gravity 1.20 or lower; with higher concentrations it is temporary, as already described. The return of the potential to zero after its disturbance by the local destruction of the film evidently indicates the formation of a new film at the scraped area. Any local disruption of the film renders that area anodal, by exposing the underly ing iron, and hence subjects it automatically to the anodal oxidizing influence. This at once reforms the film, unless the free metal is exposed over more than a certain critical area, in which case the active area spreads instead of becoming obliterated and the whole wire becomes active. Slight local disruptions, however, are at once repaired and the continuity of the film is in this manner automatically preserved. Hence the passive state is a stable one in solutions of sufficient oxidizing power.

It should be noted that this automatic tendency for the film to reform explains why the rapid removal of a considerable area of film is necessary for mechanical activation, and also the need for a brief interval between successive scrapes in the summation phenomena just described. It also explains the greater effectiveness of rapidly increasing as compared with slowly increasing currents in electrical activation. Otherwise the film may be reformed as rapidly as it is removed, and the local effect remain insufficient to start a wave of activation.

We infer therefore that the condition of equilibrium which the passive metal reaches eventually when immersed in nitric acid is one in which a thin continuous layer of oxygen compound 1 molecule in thickness covers its entire surface. There is nothing to prevent a thicker layer from being thinned by solution until it reaches this limit, but any further removal is prevented by the automatic regulatory reaction just described. In this sense the preservation of the passivating film in an oxidizing solution is the expression of a "dy-

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The brief duration of the period of activity in a wire activated in stronger solutions of nitric acid indicates a rapid reformation of the film, implying a correspondingly active local oxidation. The frequent failure of transmission in solutions stronger than 85 per cent (of 1.42 HNO₃) probably indicates a too intense oxidizing action, which interferes with the local reduction on which transmission depends. This view is confirmed by the fact, repeatedly verified throughout the present investigation, that mechanical activation is more readily induced in weaker than in stronger acid. In general, activation is favored by conditions that promote reduction (like making the metal cathodal) and hindered by conditions of the reverse type. This is illustrated by the following experiment. When two passive iron wires are placed side by side about 2 cm. apart in 60 per cent HNO₃ and connected through a key with the poles of a single Edison cell (about 0.9 volt), it is usually found, on closing the circuit, that the current is insufficient to activate the cathodal wire. During the flow of the current, however, this wire is more readily activated by scraping with a glass slide than while the current is not flowing; conversely, the anodal wire, during the flow of the current, is much more resistant to mechanical activation than before. But immediately after breaking the current the anodal wire becomes temporarily more reactive than normally—an effect due probably to its being now the cathode of the reverse or polarization current. Electrical activation is similarly modified by the passage of a constant current between a passive wire and the acid in which it is immersed; for example, while a current from five cells (about 4.5 volts) was passing through a passive wire anode immersed in 70 per cent HNO₃, touching with zinc caused a local activation which was conducted for only a few centimeters from the region of contact; after the current was broken the wave was transmitted as usual for the whole length of the wire. All the above effects indicate how closely the behavior of passive wires depends upon the condition of the surface film and upon the rate and character of the chemical
processes occurring at the surface of the metal. The parallelism of these physical effects to the phenomena of electrotonus in irritable living tissues is evident. Either facilitation or hindrance of the processes of physiological activation and conduction may result by altering the electrical polarization of the cell surface through a constant current, the effect varying according to the degree and orientation of the polarizing influence; and the above experiments show that the same is true of the film-covered metallic system.

It is remarkable how closely the behavior of passive iron wires during the period immediately following repassivation simulates that of partially narcotized or asphyxiated nerves, or of nerves in which some other kind of "block" is established. The "decrement" type of transmission characteristic of such wires is also shown by normal or completely transmissive passive wires under certain special conditions, e.g. in the neighborhood of a piece of platinum or other noble metal in close contact with the wire. Such contact invariably retards or prevents the passage of an activation wave started in another region. The explanation of this interference is simple; platinum is nobler in the electrochemical scale than passive iron; hence near the contact there exists a local circuit in which the iron is anodal, a condition which, as already described, interferes with activation and transmission. The following experiment will illustrate. If a piece of platinum wire or foil is placed across the middle region of a passive wire immersed in HNO₃ (of 60 to 80 per cent) and pressed into close contact by means of a glass rod, an activation wave started at one end of the wire is typically blocked at the region of contact and fails to enter the region beyond. The stoppage of the wave is not abrupt, but occurs with a progressive retardation which is plainly visible at a distance of 1 or 2 cm. from the contact. With an insufficiently close contact (i.e. too small a contact area) the block may not be complete; in such a case the activation wave is often observed to undergo marked retardation—at times almost stopping—at the contact; but after passing this region it regains its former speed, at first by a visible acceleration, and travels in the usual manner to the end of the wire. The parallel to a partial block in a nerve, due to local mechanical or chemical treatment, is evident; in this case also there is retardation in the altered region (or region of decrement), and, if the excitation
wave emerges from this region into the normal region beyond, it there
regains its former velocity and other characteristics. The conditions
in the passive wire suggest that a block resulting from local injury
or constriction in a nerve is due mainly to the influence of the local
current (or injury current) between the altered and the unaltered
regions—just as the platinum blocks the activation wave in a passive
wire by interposing in its path a local circuit in which the iron is
anodal and hence resistant to activation. In the metallic system par-
tial compensation of the current of the approaching active-passive
circuit by means of the current of the local Pt-Fe circuit is probably
also a factor in the extinction of the wave. Analogous conditions
may be presumed to exist in the living tissue.

A fully recovered passive wire exhibits an “all or none” type of
behavior, in this respect also resembling a normal nerve; while any
region of a passive wire which has only partially recovered is one in
which an activation wave is conducted with a decrement. Such a
local region of decrement may be produced at any desired position
in a wire which is elsewhere completely transmissive by the simple
method of touching the wire locally with a piece of zinc at an appro-
priate interval after the passage of a normal activation wave. A local
region of temporary activity is thus produced, beyond whose limits
the wire remains unaffected. This local region continues to conduct
with a decrement at a time when the remainder of the wire has com-
pletely recovered. For example, in 65 per cent acid the recovery
of complete transmissivity usually occupies between 4 and 5 minutes
at 20°; at 2 minutes after a previous complete activation a new wave
travels (on an average) for about 4 cm. from the point of contact.
If at this time one touches the wire at a central point with zinc, there
is formed a sharply defined newly activated region about 8 cm. in
length, which 3 minutes later, at a time when the rest of the wire has
recovered completely, still conducts with a decrement. An activa-
tion wave which is then started at one end of the wire will travel to
this region of decrement and penetrate the latter (usually with a
visible progressive retardation) for a variable distance of some centi-
meters. In a certain proportion of cases, if the time relations are

11 Adrian, E. D., J. Physiol., 1913, xlv, 389.
properly adjusted, the penetration is complete; and the wave, on emerging into the completely transmissive region beyond, recovers its former velocity and continues to the end of the wire. An activation wave will in this manner penetrate two regions of decrement separated by an interval of complete transmissivity, while it will be blocked by a single continuous region of a length equal to the sum of the other two. Such an experiment is closely comparable with Adrian's well known experiment in nerve.\textsuperscript{11}

It is, however, difficult, on account of the variable behavior of different iron wires, to reproduce this result at will with the above method. The following procedure is more satisfactory and gives the result just described in a large proportion of cases. Instead of producing as above a region of decrement in a single continuous wire, three separate lengths of wire are used, bent in one plane as in the diagram (Fig. 2). Good contact between any two wires can be secured by resting one bent end across the other so that the right-angled pieces are in contact and the long portions in a straight line. In such an arrangement with two completely transmissive wires an activation wave travels from the end of one wire to the end of the other without appreciable retardation at the junction, and the two wires behave like a single wire of double length. The experiment is performed as follows. The three lengths of wire (first rubbed bright and clean) are passivated in the usual manner and transferred to a dish containing acid of 65 to 70 per cent strength; they are now in a com-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{wire_setup.png}
\caption{Form and arrangement of wires in the experiment showing the difference in transmissivity between continuous and discontinuous decrement areas. See text.}
\end{figure}
completely transmissive condition and conduct activation rapidly from end to end. A region of decrement 4 cm. long is now made in each of the long wires A and C as indicated; this is done by pressing a piece of platinum foil against the wire at a point 4 cm. from the bent end and then touching this end with zinc; the wire is thus activated from its extremity to the edge of the platinum contact, and this recently activated stretch (the shaded area in Fig. 2) acts as a region of decrement for a period of several minutes. Wire B is used as a bridge between wires A and C as indicated; it is left unchanged; i.e., is completely transmissive. When wires A and C are placed end to end, as in Fig. 2, X, there is a continuous region of decrement 8 cm. long; at a certain interval after the previous activation recovery in this stretch has advanced so far that a wave started at the free end of either wire will usually traverse ac for a distance of 6 to 7 cm.; i.e., will cross the junction but fail to penetrate the whole region of decrement. The time required to reach this condition in 70 per cent acid is usually 6 to 7 minutes. The effect of interposing a completely transmissive region between wires A and C—as indicated in Fig. 2, Y. In this case the wave, started at the free end of A, typically passes along the whole three wires to the extremity of C. In favorable experiments the retardation in the decrement region of A and the recovery of speed in the bridge B are plainly visible; the activation wave on entering C is then able to pass entirely through its decrement area to the end.

It is evident that the activation wave loses steadily in penetrative power—or what might be called intensity— as it passes along the recently activated stretch or region of decrement; and regains this power when it enters the completely transmissive stretch beyond. This is the type of behavior also observed in a nerve fiber, as Adrian has shown. In the wire the variations in transmissive power are

\[\text{footnote}{Lucas points out that the only definite numerical measure, at present known, of the "intensity" of a nerve impulse is the distance which it can travel along a region of known decrement (Lucas, K., Conduction of the nervous impulse, New York, 1917, Chapter II).}\]
dependent on variations in the condition of the surface film; and it is
to be inferred, if the general conditions determining transmission are
similar in the living system and the metallic model, that the same is
true of the conducting protoplasmic strand or nerve fiber; i.e., that
the decrement-producing anesthetic acts by modifying the condition
of the protoplasmic surface film. 13

As Lucas and Adrian have pointed out, conduction with a decre-
ment is undoubtedly a physiologically normal phenomenon in many
regions of the central nervous system, as well as in the myoneural
junctions and other nerve endings and synapses. 14 Whether a con-
ducting element or combination of elements in the living organism
transmits excitation in the “all or none” manner or with a decrement
depends not only upon its special peculiarities of structure or organi-
ization but also upon its physiological condition—state of metabolism,
fatigue, etc.—at the time. There is much independent evidence that
protoplasmic excitation and transmission are in general dependent
on local and transmitted alterations of the protoplasmic surface films
or plasma membranes under the influence of the local bioelectric cur-
rrents accompanying activity. If this is true, conditions changing the
properties of these films must influence the whole behavior of the pro-
toplasmic system. The phenomena of anesthesia in particular seem
to afford many instances of this kind of correlation. 13

In living animals the time relations of the recovery process in the
different irritable cells and tissues vary widely, and they usually
exhibit a close correlation with the time relations of the respective
excitation processes. In most cases recovery is more rapid in the
living tissue than in the passive iron model; yet this is not always the
case. In the photoreceptors of Mollusca recovery may require sev-
eral minutes, and in the smooth muscle of the mammalian ureter
Engelmann found under some conditions imperfect transmission for
15 seconds or more after the passage of a contraction wave. 15 The

13 The evidence that the anesthetic acts primarily upon the plasma membrane
of cells is summarized in my review, The theory of anaesthesia (Lillie, R. S.,
14 Lucas, K., Conduction of the nervous impulse, New York, 1917, Chapters
X and XIII.
high velocity of the recovery process in highly irritable tissues like nerve, where the relative refractory period lasts for only a few thousandths of a second, must be referred to special peculiarities of structure and metabolism whose detailed nature is entirely unknown at present.

SUMMARY.

1. Passive iron (steel) wires, when activated after prolonged immersion in nitric acid of 55 to 90 per cent concentration (volumes per cent of HNO₃, specific gravity 1.42) revert spontaneously to the passive state, after a temporary reaction which is transmitted rapidly over the whole length of wire. The duration of this reaction at any region decreases rapidly with increase in the concentration above a certain critical limit of 52 to 54 per cent. In weaker acid (50 per cent and lower) the reaction continues uninterruptedly until all the metal is dissolved.

2. Immediately after this automatic repassivation the wire fails to transmit activation through more than a short distance (1 to 2 cm.), if left undisturbed in the acid it recovers by degrees its power of transmission (as measured by the distance traveled by an activation wave), at first slowly, then more rapidly; eventually, after an interval varying with the concentration of acid and the temperature, the activation wave is transmitted through an indefinite distance as before.

3. The return of complete transmissivity in 55 per cent acid occupies less than a minute (at 20°); in stronger acid it is more gradual, requiring in 90 per cent acid 20 minutes or more. This "complete recovery time" is nearly proportional to the excess of concentration of acid above the limiting value of 53 to 54 per cent.

4. In a given solution of acid the rate of recovery exhibits a temperature coefficient closely similar to that of most chemical reactions at this temperature (3-20°), and also to that of the rate of recovery (refractory period) of irritable living tissues after stimulation (Q₁₀ = about 3).

5. Two definite phases are distinguishable in the recovery process: (1) the redeposition of the continuous passivating surface layer (of oxide or oxygen compound); and (2) the progressive change of the newly passivated wire from the state of incomplete to that of complete
transmissivity. The former phase is of brief duration and is indicated by a sudden change in the electrical potential of the wire, from that of active to that of passive iron; this phase is succeeded by the second and more prolonged period during which the passivating layer undergoes the progressive alteration associated with the recovery of transmissivity. This alteration appears to consist in a progressive thinning of the passivating film until a minimal thickness of (probably 1 molecule) is attained. Further thinning is prevented by local electrochemical oxidation.

6. The phenomena of partial or limited transmission during the second phase of the recovery process show a close correspondence with the phenomena of conduction with decrement in irritable living tissues such as nerve. Other analogies with the behavior of irritable tissues (threshold phenomena, distinction between "local" and "propagated" effects, summation, effects resembling electrotonus) are described.