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

PART I.

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I. INTRODUCTORY.

A striking feature in the phenomena of activation in passive iron wires immersed in solutions of nitric acid is that in acid above a certain critical concentration the reaction is a temporary one, followed immediately by an automatic return of the metal to the passive state. Activation initiated at any region of such a wire is thus transmitted rapidly along its whole length in a wave-like manner, each region as it becomes active activating the region next adjoining (by means of the local electric circuit between the passive and active areas) and immediately becoming itself again passive. In this tendency to revert promptly to the chemically inactive or passive state after activation the passive metal resembles an irritable and conducting living element such as a nerve fiber or muscle cell. In order to maintain activity in the living system, constant repetition of stimulation is necessary; and similarly chemical activity in a passive wire immersed in a sufficiently strong solution of nitric acid (55 or more volumes per cent of HNO₃, specific gravity 1.42) is an automatically self-limiting process which can be maintained only by repeated contact of the activating metal; e.g., zinc. Even under such conditions only a partial and irregular activity is possible, which is confined to the immediate neighborhood of the contact; i.e., it fails to be transmitted through more than a short distance. This behavior is highly

1 For a fuller description of this phenomenon cf. Lillie, R. S., Science, 1918, xlviii. 51.
characteristic; after a wire has been activated in the usual manner and has reverted to the passive state it is found impossible to reactivate it as a whole by a single contact until a certain interval has elapsed, the duration of which varies with the concentration of acid and with the temperature in a manner to be described later. At first, touching with zinc causes only a brief local reaction which is confined to an area of 1 or 2 cm. from the contact; a second trial made somewhat later gives a reaction which spreads more rapidly and through a greater distance; and with further successive trials the distance through which the activation wave travels, as well as its speed, increases by degrees until eventually rapid transmission through an indefinite distance becomes again possible.

This failure of complete activation and transmission for a certain period succeeding the passage of an activation wave may be compared with the similarly inexcitable and non-conductive interval or "refractory period" of irritable living systems. It is well known that a decline or disappearance of irritability and conductivity during a certain interval succeeding the response to stimulation is a constant feature of the excitation process in all irritable tissues. The duration of this interval varies with the nature of the tissue; the most notable correlation is that it is brief in tissues with rapid rate of response (i.e. brief chronaxie), such as voluntary muscle and nerve, and relatively prolonged in slowly responding tissues like the heart or involuntary muscle. In certain cases, as in the photoreceptors of mollusks, the period of diminished sensitivity following the response may last for several minutes, such a phenomenon suggests a fatigue effect, and there are various significant resemblances between the refractory period and cases of brief or evanescent fatigue; thus the period is lengthened by conditions which delay recovery from fatigue, such as lack of oxygen, and also by repeated stimulation, as shown in the


3 For a description of this phenomenon cf. Hecht, S., J. Gen. Physiol., 1918-19, i, 545.

prolonged "compensatory pause" following an "extra-contraction" in heart muscle.

It is generally assumed that the refractory phase corresponds essentially to the period required for recovery or recuperation. The act of stimulation appears to involve the more or less complete breakdown or removal of some material or structure which is essential to stimulation; the refractory interval represents a period of reconstruction or restoration. When this process of repair is rapid the refractory period is brief, and vice versa. In any single tissue the rate of this reconstruction exhibits a general parallelism with the rate of the structural or chemical breakdown associated with stimulation; hence rapidly responding tissues have as a rule brief refractory periods. This parallelism can, however, be artificially disturbed, as in Tait's experiments, by drugs like protoveratrine and yohimbine which abnormally prolong the refractory period. In such cases an abnormal prolongation of the descending or return phase of the bioelectric variation is also observed. There appears thus to be a correlation between the length of the refractory period and the duration of the bioelectric variation, especially of the return phase of the latter. The relation, however, is not simple, for it is certain that in some cases, e.g. heart muscle, the whole period of diminished excitability (including both the "absolute" and the "relative" refractory phases) may greatly outlast the electrical variation. This is also true of the metallic model under consideration in the present paper. It is thus not sufficient to regard the entire refractory phase as corresponding to the time required to restore the normal or "resting" semipermeability and polarizability of the altered plasma membranes of the irritable elements. Recovery of semipermeability is no doubt necessary to a recovery of irritability, since electrical stimulation requires polarizability in the membranes; but some further change appears also to be essential. This question will be discussed later, after the processes in the metallic model

6 Tait, J., Quart. J. Exp. Physiol., 1910, iii, 221.
6 Trendelenburg, W., Arch. ges. Physiol., 1912, cxliv, 39. The case of nerve, with a brief refractory period, is similar (cf. Adrian, E. D., J. Physiol., 1914, xlviii, 453).
7 The inference from the work of Nernst, Lapicque, Lucas, Hill, and others on electrical stimulation.
have been considered. It seems probable that the presence of a brief "absolute," preceding a longer "relative," refractory phase is an index of the existence of two distinct stages or processes in the reconstitution of the plasma membrane, the first stage preceding and the second succeeding the recovery of semipermeability. This view, however, accords imperfectly with Tait's special hypothesis that the "absolute" refractory period corresponds to the period of upstroke of the bioelectric variation, and the "relative" period to the return phase.

In the metallic model the change of potential accompanying repassivation, i.e. the return phase of the whole electrical variation associated with the local reaction, is a definite index of the reformation of the passivating surface film of oxygen compound. This process occurs rapidly; but it is not until the lapse of a considerable time (usually some minutes) after its completion that the condition of the film becomes such as to permit again of ready and complete transmission. Evidently some further change in the newly restored film is necessary for a return of its original properties; and it seems probable that in the living system closely comparable conditions may obtain. It is certain that the relative refractory period greatly outlasts the return phase of the bioelectric variation in many cases.

In the living irritable element there is evidence that stimulation is associated with a temporary alteration or breakdown of the protoplasmic surface film or plasma membrane, involving a general increase of permeability. Stimulation follows any sufficiently rapid and extensive change in the electrical polarization of the semipermeable protoplasmic surface, or any sufficient local mechanical or chemical alteration; such a change, even though purely physical in itself, initiates a chemical disturbance, associated with a variation of potential, which sweeps over the cell surface, and apparently consists essentially in a wave of alternate dissolution and reconstruction of the surface film. This "propagated disturbance" is the condition for the release of the chemical and other activities in the cell interior which constitute

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8 For a brief summary of this evidence cf. Lillie, R. S., Am. J. Physiol., 1915, xxxvii, 356. Further references there given.

9 Keith Lucas' term, to distinguish the transmitted effect from the local or initiatory effect produced by the stimulating agent. For the experimental basis of this distinction cf. Adrian, E. D., and Lucas, K., J. Physiol., 1912, xlv, 68.
the response to stimulation. Normally in a highly irritable element, such as a muscle cell or nerve fiber, the whole cell surface is thus involved, hence the "all or none" character of the response; but the passage of the excitation wave, and with it the local response, can be interfered with or prevented by various artificial conditions (narcosis, electrotonus, local chemical or mechanical conditions). There are many purely physiological indications that the transmission of excitation from one region of the conducting element to the next adjoining is due to the local bioelectric variation resulting from this surface alteration. The reference of the bioelectric variation to a local change in the physical and chemical character of the cell surface, which apparently acts like an electrode of variable chemical composition and potential, is consistent with what we know of the conditions in various inorganic systems exhibiting an analogous type of behavior; examples of such systems are mercury in hydrogen peroxide, chromium and other electrodes exhibiting rhythmical changes of potential, and especially metals in the passive state, more particularly iron.

Activation and transmission in passive iron are due to alterations in the continuous or impermeable surface film of oxidation product covering the surface of the metal. On account of the extreme thinness of this film, the surface of the passive metal, in its property as an electrode, is highly variable and sensitive to mechanical or other disturbance. The susceptibility of a passive iron wire to activation by mechanical and chemical agents and by the electric current (when the metal is made cathode) is thus readily explained. Interruption of the film produces a local circuit, and electrolyses at the electrode areas of this circuit—reduction at the cathodal and reoxidation at the anodal areas—are responsible both for the rapid extension of the active area (transmission) and for the automatic return to the passive

11 Ostwald, W., Z. physik. Chem., 1900, xxxv, 33, 204.
12 The general article by Bennett and Burnham (Bennett, C. W., and Burnham, W. S., J. phys. Chem., 1917, xxi, 107) gives a full account of the phenomena of passivity in metals and an exhaustive literature list.
13 I. e. impermeable to acid, hence its protective influence.
state. The resemblances between the phenomena of activation and transmission in the passive iron model and in living protoplasm are thus to be referred to the presence, in both systems, of surface films which readily undergo chemical and structural alteration, these alterations producing changes in the electromotor properties of the surface. Such local alterations have further chemical effects, since they produce local electric circuits which furnish the conditions for electrolysis, and these chemical effects are often extensive because of their automatic tendency to spread wherever a continuous and uniform surface film is present.

The general biological significance of these properties of surface films, especially in relation to the film-pervaded or emulsion-like structure of living protoplasm—emulsions being systems whose properties are determined by the presence of surface films of soap or other material—will be partly evident from the foregoing, but will not be considered in detail in the present paper. It is essential to note, however, that recovery of irritability after stimulation depends (on the foregoing theory) upon the restoration of the altered protoplasmic surface film to its previous condition. It seems most likely that an essentially new film is formed after each stimulation; this process of reconstruction probably involves a specific chemical resynthesis, in addition to a purely physical process of redistribution or rearrangement of surface active compounds. The importance of the chemical factor is indicated both by the dependence of recovery on oxygen and by its high temperature coefficient. In the passive iron model the factors in the recovery of transmissivity are simpler than in protoplasm; but repassivation is known to depend upon the formation of a new surface film of oxidation product; and immediately after the redeposition of this film its properties are different from those which it attains later. We can in fact clearly distinguish two distinct processes in the recovery of passive iron; one the redeposition of the film, and the other the progressive alteration of the newly deposited film until the final state of complete transmissivity is attained. The first process

14 For an account of various biological analogies in the behavior of the surface film of passive iron, cf. Lillie, R. S., Science, 1919, 1, 239, 416.
is associated with a change in the electrical potential of the metallic surface, from that characteristic of active iron (in contact with acid) to that of the passive or oxide-covered surface. This variation of potential is a direct and readily observable index of the return to the passive state; it occurs simultaneously with the decline and cessation of the reaction (effervescence, etc.) and lasts for only a short time, e.g. a fraction of a second; the succeeding phase of gradually returning transmissivity is much more prolonged. A somewhat similar division of the recovery process into two stages can also be distinguished in living tissues, especially those with relatively long refractory periods, e.g. heart muscle, as already indicated. These resemblances justify the belief that a study of the conditions of recovery in the metallic system may throw light on the general nature of the recovery process in living protoplasm.

II. Phenomena of Automatic Repassivation in Iron Wires.

The following account is based on experiments with iron wires of standard composition and properties, known as "music steel wires," manufactured by the Spencer Wire Company of Worcester, Massachusetts. Wires of 1 to 1.2 mm. diameter were used (Nos. 20 and 25). The metal is bright, elastic, and highly tempered. Its behavior in nitric acid of different concentrations is definite and regular, within certain well defined limits of variation to be described below. It is important in experiments of this kind to use metal of uniform quality, for ordinary specimens of iron (e.g. "black iron" sheeting, soft iron wire, wire nails, etc.) are often highly variable and capricious in their manner of reaction with strong nitric acid.

I have already described briefly the appearances accompanying the activation of these wires in different dilutions of pure nitric acid. Before use, the freshly cut wires are allowed to react for 15 seconds or so with dilute acid (specific gravity 1.2); they are then rinsed in water, wiped clean with a coarse cloth, and passivated by immersion in strong HNO₃ (specific gravity 1.42). The passive wires are steel bright and undergo no change if left undisturbed in dilute nitric acid (from specific gravity 1.2 up). When they are activated in dilute acid, e.g. by touching with zinc or scraping with glass, there is an
immediate darkening of the bright surface (from formation of oxide),
followed by active effervescence; both of these changes then spread
rapidly along the whole length of the wire. A completely transmis-
sive wire thus reacts as a whole, in a manner which in acid of a defi-
nite concentration and temperature is constant and independent of
the mode of activation. The reaction continues for an indefinite
time in acid below a certain concentration; this critical concentration
is about 50 volumes per cent of 1.42 HNO₃ (equal to acid of 1.2 specific
gravity or about 7.5 N by volume); in all stronger solutions the reac-
tion soon comes automatically to rest and passivity is regained. In
such cases the duration of the local reaction varies in a characteristic
manner with the concentration of HNO₃; e.g., in acid of 83 volumes per
cent (about 12 N by volume) effervescence lasts (at 20°) for only a
small fraction of a second, while in 55 per cent HNO₃ it continues for
several seconds, at first uniformly and later declining and finally ceas-
ing somewhat abruptly, usually after 6 to 8 seconds. During the
reaction a dark brown oxide is deposited on the surface of the metal;
the thickness of this coating depends on the duration of the reaction;
hence immediately after spontaneous repassivation in 55 per cent
acid a wire is almost black in color, while in 80 per cent acid it is only
slightly bronzed. This deposit gradually dissolves away if the metal
is left in the acid; it is loosely adherent and is entirely distinct from
the thin, resistant, and invisible surface film which imparts passivity.
The recently formed oxide-covered region furnishes a convenient indi-
cator of the distance traveled by the activation wave in cases of par-
tial transmission, since its boundary against less recently activated
regions is always sharply defined.

On activation the potential of the metal changes suddenly from that
characteristic of passive to that of active iron; in nitric acid of the
above concentrations the active metal is more negative (zinc-like or
anodal) by 0.7 to 0.8 volt. Hence the duration and certain other
features of the reaction can be observed conveniently by the use of
a voltmeter or string galvanometer. When two iron wires, bent into
an appropriate shape and connected through keys to a voltmeter (pref-
erably one with a scale of 1 to 2 volts and a central zero), are pas-
vivated by dipping into 1.42 HNO₃, and are then placed side by side a
short distance apart in a flat dish containing 55 per cent acid, on
activating one of the wires the needle of the instrument shows at once a rapid initial excursion of about 0.7 volt. During the continuation of the reaction the potential exhibits irregular rhythmical fluctuations about this point; later, as the reaction begins to decline, it decreases by degrees, finally swinging back rather abruptly to zero and a little beyond as the reaction ceases. It is characteristic that immediately after repassivation the wire is always slightly more positive than before, by a potential of 0.01 to 0.02 volt, and remains in this condition for some time; by degrees, especially if the acid is stirred, the wire resumes its original potential. The rhythmic variation of potential is an especially interesting peculiarity from the biological point of view, since rhythmicity of a similar kind is frequent in irritable living tissues, as well as in other film-covered inorganic systems, such as mercury in hydrogen peroxide. It indicates a tendency in the early stages of the reaction to an alternating formation and disruption of the passivating film; later the process of formation predominates and the film becomes continuous over the whole surface; the wire is then passive. The "after-positivity" has an analogy to the so called "positive after-variation" observed under certain conditions in nerves after stimulation; from the most general point of view it is to be regarded as a polarization effect of the kind found at all polarizable electrodes.

Time Relations of Recovery of Transmissivity.—The behavior of a wire in nitric acid of 60 per cent concentration will first be described for illustration. When such a wire, after having been left undisturbed in this solution for some time (e.g. an hour), is touched at one end with zinc a wave of activation sweeps rapidly (at some hundred centimeters a second) over its whole length; after 1 or 2 seconds the reaction ceases and the metal becomes again passive. For some minutes after repassivation the wire is found to be incapable of transmitting activation for more than a limited distance. At the very first, touching with zinc produces only a slight local reaction; when touched 30 seconds later the local effervescence and darkening caused by the zinc are somewhat more pronounced, and the reaction spreads slowly for 2 or 3 cm. from the contact; after 1 minute there is somewhat more rapid transmission through 4 or 5 cm.; after 2

minutes the speed is still greater and the distance has increased to 10
or 15 cm.; and after 3 minutes the wave usually travels rapidly (though
less so than before the original activation) over the whole length as
before. Recovery is thus a gradual process whose course can be
traced by measuring the distance which an activation wave travels
at successive intervals after repassivation. In the experiments about
to be described the relation between the concentration of acid and the
rate of recovery has been determined in this manner for solutions of
nitric acid of different concentration.

The procedure has been as follows. Straight lengths of wire 20
cm. long are bent at one end into a hook shape (to facilitate handling,
which is done with glass hooks and rods) and treated as already de-
scribed so as to secure a uniform surface; they are then passivated by
immersion in strong nitric acid (Baker’s “Analyzed,” specific gravity
1.42), where they may remain for an indefinite time before using. The
same wires may be used over and over again in different experiments.
In each experiment with a given solution several such wires, e.g., ten,
are placed side by side in a flat-bottomed rectangular glass dish (23
by 14 cm.) containing the acid; when all the wires are in position they
are activated simultaneously (or nearly so) by touching at one end
with a bar of zinc; an activation wave then sweeps rapidly over each
wire, which receives at the same time a coating of the brown oxide.
The wires are now again passive, but at first transmit activation im-
perfectly, as just described. The distance traveled by the activation
wave after a definite time interval of recovery is now determined by
touching the ends of the wires with zinc, one by one, in succession
from left to right at regular intervals. For instance, in 65 per cent
acid the successive wires are activated at ½ minute intervals; a series
is thus obtained showing the distances traveled after periods of recov-
er lasting respectively ½ minute, 1 minute, 1½ minutes, 2 minutes,
etc. The distances can readily be measured with a millimeter rule;
the limit of each freshly activated area is distinctly marked by the
dark shade of the more recently deposited oxide; this boundary re-
mains visible for some time after the reaction, so that if desired the
measurements can be made at leisure at the conclusion of a series of
experiments.
The rate of recovery, as measured by the gain per unit of time in the traveling power of the wave, is at first gradual and then more rapid. Transmission for the full distance of 20 cm. is equivalent to transmission for an indefinite distance; it is in fact unusual for a wave that has traveled 16 cm. (at 20°) to fail to travel the whole length of any wire. Transmission for 20 cm. thus signifies full or complete transmissivity. If we define transmissivity in numerical terms as the distance in centimeters which the wave is capable of traveling along a homogeneous wire before spontaneous extinction, its values range from unity or less to infinity, the latter value signifying transmission without progressive decline in traveling power. This condition corresponds to an “all or none” behavior, or conduction without decrement, in a living conducting tissue like nerve; partial transmission is equivalent to conduction with a decrement; the numerical measure of this decrement may be defined as the reciprocal of the distance traveled before extinction.

The behavior of different wires under otherwise identical conditions is subject to considerable variation, due apparently to accidental differences in the structure of the metal in the different wires. Thus there are occasional exceptions to the rule of an increase in the distance of transmission on passing from one member of a series to the next. Table I gives the results of seventeen separate series of determinations with wires immersed in 65 volumes per cent of 1.42 acid (= about 9 N by volume). These series were all carried out on a single day, using two sets of ten wires each; these were used alternately, a determination with the one set being made while the other was undergoing repassivation in strong acid. There are thus eight series of observations with the one group and nine with the other; the wires were placed in random order in each series; i.e., no care was taken to treat each wire individually as in the experiments to be described later. The figures give the distances in centimeters traveled by the activation wave along the wire when the latter is touched at one end with zinc after the intervals (since the previous complete activation) given at the head of the column. Each horizontal line gives the observations with a single series. The temperature of the acid was constant between 20 and 21°.
TRANSMISSIVITY IN PASSIVE IRON WIRES

It will be observed that complete recovery occupies about 4 minutes in this solution; in three series (four wires) transmission was complete after \(3\frac{3}{4}\) minutes; twelve series (eighteen wires) required 4 minutes, and two \(4\frac{1}{2}\) minutes. The average distance of transmission at the end of each interval is given at the foot of the column. The increment (per unit of time) of transmissivity during the whole recovery period of 4 minutes is at first gradual and more rapid later. The transition from a limited to an unlimited transmissivity occupies a comparatively short interval toward the end of the period. This

<table>
<thead>
<tr>
<th>Concentration of HNO(_3), 65 Volumes Per Cent. Temperature 20-21°C.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Series</th>
<th>Intervals since previous activation</th>
<th>Distance traveled</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>½ min.</td>
<td>1 min.</td>
</tr>
<tr>
<td>A</td>
<td>2.6</td>
<td>4.0</td>
</tr>
<tr>
<td>B</td>
<td>2.6</td>
<td>4.2</td>
</tr>
<tr>
<td>C</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>D</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>E</td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>F</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>G</td>
<td>2.0</td>
<td>3.7</td>
</tr>
<tr>
<td>H</td>
<td>2.5</td>
<td>3.9</td>
</tr>
<tr>
<td>I</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>J</td>
<td>1.7</td>
<td>2.4</td>
</tr>
<tr>
<td>K</td>
<td>2.4</td>
<td>4.3</td>
</tr>
<tr>
<td>L</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>M</td>
<td>4.5</td>
<td>4.7</td>
</tr>
<tr>
<td>N</td>
<td>2.0</td>
<td>3.1</td>
</tr>
<tr>
<td>O</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>P</td>
<td>1.9</td>
<td>2.3</td>
</tr>
<tr>
<td>Q</td>
<td>2.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Average</td>
<td>2.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
feature of the behavior has an important general significance, as will be seen below.

The same type of behavior was found in all the solutions used, which included nitric acid of the following concentrations (in volumes per cent of 1.42 HNO₃): 55, 57.5, 60, 65, 70, 75, 80, 85, 90. The time required for complete recovery of transmissivity increases rapidly with increasing concentration of acid. Table II gives the typical recovery times for different solutions at 20°. In the most concentrated solutions, 85 and 90 per cent, especially the latter, the recovery process may exhibit irregularities whose explanation is not entirely clear; and at times transmissivity remains incomplete, even after hours or days in these solutions. Apparently very strong acid renders the surface film resistant to alteration under certain conditions. Frequently, however, there is complete recovery in 90 per cent or even stronger acid; but the time required is usually 20 minutes or more. In the lower concentrations complete transmissivity always returns within the time indicated in Table II.

In their general character the measurements for the different solutions resemble those given in Table I, so that it is unnecessary to reproduce them in detail; Table III, however, gives the averages obtained for the different solutions from 57.5 per cent on. In these

<table>
<thead>
<tr>
<th>Concentrations (1.42 HNO₃)</th>
<th>Time for complete recovery (20°).</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol. per cent</td>
<td></td>
</tr>
<tr>
<td>55.0</td>
<td>30 - 45 sec.</td>
</tr>
<tr>
<td>57.5</td>
<td>60 - 70 &quot;</td>
</tr>
<tr>
<td>60.0</td>
<td>90 -110 &quot;</td>
</tr>
<tr>
<td>65.0</td>
<td>34 - 4 min.</td>
</tr>
<tr>
<td>70.0</td>
<td>6 - 7 &quot;</td>
</tr>
<tr>
<td>75.0</td>
<td>9 - 10 &quot;</td>
</tr>
<tr>
<td>80.0</td>
<td>12 - 13 &quot;</td>
</tr>
<tr>
<td>85.0</td>
<td>14 - 16 &quot;</td>
</tr>
<tr>
<td>90.0</td>
<td>18 - 20 &quot; (or more).</td>
</tr>
</tbody>
</table>

17 Exact measurements with 55 per cent acid are difficult to make because the wire at the end of the reaction (which lasts 5 or 6 seconds) is so covered with oxide that the distance traveled by a later activation wave is not distinctly marked. Recovery is more rapid and the whole behavior is less regular than in the stronger solutions.
### Table III

Average distances traveled by activation wave in each solution at definite intervals after previous activation.

<table>
<thead>
<tr>
<th>Concentration of acid</th>
<th>sec.</th>
<th>cm.</th>
<th>sec.</th>
<th>cm.</th>
<th>sec.</th>
<th>cm.</th>
<th>sec.</th>
<th>cm.</th>
<th>sec.</th>
<th>cm.</th>
<th>sec.</th>
<th>cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.5</td>
<td>10</td>
<td>3.4</td>
<td>20</td>
<td>6.5</td>
<td>30</td>
<td>9.6</td>
<td>40</td>
<td>11.3</td>
<td>50</td>
<td>14.0 (Full transmission in 4 wires out of 19.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.0</td>
<td>12.6</td>
<td></td>
<td>80</td>
<td></td>
<td>12.7</td>
<td></td>
<td>90</td>
<td></td>
<td>13.4 (5 full in 19.)</td>
<td>100</td>
<td></td>
<td>16 full in 19.</td>
</tr>
<tr>
<td>65.0</td>
<td>3</td>
<td>2.7</td>
<td>1.3</td>
<td>1.5</td>
<td>3.7</td>
<td>2.3</td>
<td>4.6</td>
<td>2.2</td>
<td>6.2</td>
<td>3.7</td>
<td>7.3</td>
<td>3.7</td>
</tr>
<tr>
<td>70.0</td>
<td>12.7 (4 full in 16.)</td>
<td>60</td>
<td>10.1 (2 full in 14.)</td>
<td>6</td>
<td>10.1 (9 full in 12.)</td>
<td>13</td>
<td>All full.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75.0</td>
<td>6.7</td>
<td></td>
<td>5.9</td>
<td></td>
<td>5.9</td>
<td></td>
<td>5.9</td>
<td></td>
<td>5.9</td>
<td></td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>10.1</td>
<td></td>
<td>9.7</td>
<td></td>
<td>9.7</td>
<td></td>
<td>9.7</td>
<td></td>
<td>9.7</td>
<td></td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>85.0</td>
<td>10.3 (3 full in 17.)</td>
<td>13</td>
<td>All full.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90.0</td>
<td>12.8 (2 full in 14.)</td>
<td>15</td>
<td>12.4 (5 full in 13.)</td>
<td>16</td>
<td>13.9 (2) (4 full in 6.)</td>
<td>19</td>
<td>13.9 (2) (4 full in 6.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
experiments the intervals between the successive activations in any series were adjusted to the time period of recovery characteristic of the solution used, as given in Table II. In each series (with a few exceptions) ten wires were used, with the procedure already described. The number of separate determinations for each of the average distances given in Table III varied from twelve to nineteen (in a few cases more), except in those cases where part of the wires had recovered completely in the time allowed; in these cases the number of determinations is given in brackets. When plotted with distances as ordinates and times as abscissae the data give curves of an hyperbola-like form, beginning with a horizontal and ending with a vertical course (Fig. 1).

Fig. 1. Distances traveled by activation wave in different solutions of HNO₃ at different intervals after a previous complete activation in the same solution. Ordinates are distances (cm.); abscissae are times (minutes) elapsed since the previous activation. A single curve represents the behavior in acid of the concentration indicated at the end of the curve (in volumes per cent of HNO₃, sp. gr. 1.42) at 20°. The small circles represent the averages given in Table III.
All these determinations were made at room temperature, and the
temperature of the acid was taken at the end of each series; in all but
seven of the 119 series summarized in the table the temperature was
between 19 and 21°; in the others it rose to 21.5 or 22° (in one case
22.5°). The irregular fluctuations in the series have, however, noth-
ing to do with temperature, but are to be referred chiefly to accidental
variations in the surface structure of the different wires. In order to
obviate this source of irregularity, as far as possible, a number of other
series of determinations were made later, using a somewhat different
plan. In each of these series eight wires were employed, designated
A, B, C to H; each wire during passivation was kept separately in a
long test-tube labeled with its letter, so that its individual behavior
could be observed. Eight separate series of determinations were
made as above in each of the following solutions of acid: 60, 65, 70,
75, and 80 volumes per cent, in such a manner that each wire was ex-
posed to each solution for each of the eight periods employed in the
series. For example, the times of exposure to 75 per cent HNO₃
were 2, 4, 6, 7, 8, 9, 10, and 11 minutes; in the first series with this so-
lution the wires were arranged in the acid in the order A, B, C to H
corresponding to the above times; in the second series Wire H was
shifted from the end to the beginning of the series, so that it received
2 minutes exposure before reactivation, Wire A 4 minutes, and so
on; in the third series the wires were in the order G, H, A, B to F,
etc. In this manner a record of transmission distances was obtained
for each wire with each of the eight recovery intervals allowed.

The results of these series were on the whole more regular than those
of the earlier series. The wires used were of the same kind as before,
but cut from a different roll (No. 25 thickness). The behavior and
the recovery times showed little difference from those of the earlier
series (made with No. 20 wire). Care was taken to keep the tempera-
ture constant between 19.5 and 20.5°. Table IV gives the complete
record of two typical series with 65 and 80 per cent acid respectively.

These results are closely similar to those obtained in the earlier se-
ries, and no significant differences of behavior are observable in the
individual wires. It is apparent that each reaction means a renewal
of the reacting surface, since a thin layer of metal is dissolved each
time. The irregularities of behavior are therefore probably due to
variations in the finer grain of the metal, involving irregular local potential differences which influence the local rate of reaction and interfere somewhat with the uniformity of the reaction at different regions of the surface layer. In Fig. 2 the averages for the different solutions of these series are plotted and curves drawn as before. These averages are given in Table IV.

**TABLE IV.**

<table>
<thead>
<tr>
<th>Wire.</th>
<th>Distance traveled.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intervals since previous activation.</td>
</tr>
</tbody>
</table>

**Series 1. Concentration of HNO₃, 65 volumes per cent. Temperature 20°C.**

<table>
<thead>
<tr>
<th></th>
<th>1 min.</th>
<th>½ min.</th>
<th>2 min.</th>
<th>½ min.</th>
<th>3 min.</th>
<th>½ min.</th>
<th>4 min.</th>
<th>½ min.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
</tr>
<tr>
<td>A</td>
<td>4.2</td>
<td>4.8</td>
<td>4.5</td>
<td>5.5</td>
<td>8.1</td>
<td>10.4</td>
<td>11.7</td>
<td>Full.</td>
</tr>
<tr>
<td>B</td>
<td>3.2</td>
<td>3.2</td>
<td>4.1</td>
<td>4.0</td>
<td>4.9</td>
<td>8.3</td>
<td>13.3</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>3.2</td>
<td>4.4</td>
<td>4.6</td>
<td>5.7</td>
<td>7.5</td>
<td>9.1</td>
<td>12.9</td>
<td>&quot;</td>
</tr>
<tr>
<td>D</td>
<td>4.0</td>
<td>5.2</td>
<td>4.4</td>
<td>8.3</td>
<td>7.4</td>
<td>10.2</td>
<td>11.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>E</td>
<td>2.3</td>
<td>3.5</td>
<td>4.2</td>
<td>7.1</td>
<td>10.5</td>
<td>10.3</td>
<td>13.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>F</td>
<td>2.8</td>
<td>3.9</td>
<td>4.9</td>
<td>5.9</td>
<td>8.4</td>
<td>10.5</td>
<td>15.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>G</td>
<td>3.8</td>
<td>2.5</td>
<td>5.2</td>
<td>5.9</td>
<td>9.6</td>
<td>9.9</td>
<td>12.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>H</td>
<td>3.1</td>
<td>4.5</td>
<td>5.0</td>
<td>5.5</td>
<td>7.3</td>
<td>11.0</td>
<td>15.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Average.</td>
<td>3.3</td>
<td>4.0</td>
<td>4.6</td>
<td>6.0</td>
<td>8.0</td>
<td>10.0</td>
<td>13.4</td>
<td></td>
</tr>
</tbody>
</table>

**Series 2. Concentration of HNO₃, 80 volumes per cent. Temperature 20°C.**

<table>
<thead>
<tr>
<th></th>
<th>2 min.</th>
<th>4 min.</th>
<th>6 min.</th>
<th>8 min.</th>
<th>10 min.</th>
<th>12 min.</th>
<th>13 min.</th>
<th>14 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
<td>cm.</td>
</tr>
<tr>
<td>A</td>
<td>1.2</td>
<td>1.5</td>
<td>2.3</td>
<td>3.2</td>
<td>5.2</td>
<td>13.2</td>
<td>16.8</td>
<td>Full.</td>
</tr>
<tr>
<td>B</td>
<td>1.5</td>
<td>1.8</td>
<td>2.0</td>
<td>3.4</td>
<td>6.8</td>
<td>9.4</td>
<td>Full.</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>1.9</td>
<td>1.9</td>
<td>3.1</td>
<td>3.4</td>
<td>6.4</td>
<td>11.3</td>
<td>18.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>D</td>
<td>1.7</td>
<td>2.7</td>
<td>2.7</td>
<td>3.3</td>
<td>4.5</td>
<td>8.9</td>
<td>11.6</td>
<td>Full.</td>
</tr>
<tr>
<td>E</td>
<td>1.8</td>
<td>2.5</td>
<td>2.7</td>
<td>3.8</td>
<td>6.1</td>
<td>7.6</td>
<td>14.5</td>
<td>&quot;</td>
</tr>
<tr>
<td>F</td>
<td>1.4</td>
<td>2.1</td>
<td>2.4</td>
<td>4.6</td>
<td>6.4</td>
<td>11.2</td>
<td>9.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>G</td>
<td>1.3</td>
<td>2.0</td>
<td>3.0</td>
<td>4.5</td>
<td>7.2</td>
<td>9.9</td>
<td>12.0</td>
<td>10.7</td>
</tr>
<tr>
<td>H</td>
<td>1.5</td>
<td>1.6</td>
<td>2.6</td>
<td>4.1</td>
<td>5.4</td>
<td>11.2</td>
<td>13.4</td>
<td>Full.</td>
</tr>
<tr>
<td>Average.</td>
<td>1.5</td>
<td>2.0</td>
<td>2.6</td>
<td>3.8</td>
<td>6.0</td>
<td>10.3</td>
<td>13.7</td>
<td></td>
</tr>
</tbody>
</table>

In this arrangement the horizontal lines give the results for the same wire with varying intervals before reactivation. Any single series is to be read along the diagonals from above down, beginning with the first column, in such a way that the letters fall in consecutive order.
## TABLE V.

<table>
<thead>
<tr>
<th>HNO₃</th>
<th>Distance travelled.</th>
<th>Interval since previous activation.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min.</td>
<td>cm.</td>
</tr>
<tr>
<td>60</td>
<td>1/2</td>
<td>3.7</td>
</tr>
<tr>
<td>65</td>
<td>1</td>
<td>3.3</td>
</tr>
<tr>
<td>70</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>75</td>
<td>2</td>
<td>0.0</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Fig. 2. Graphs for the second set of determinations with No. 25 wires. Otherwise as in Fig. 1. The circles represent the averages of Table V.

Fig. 3. Relation between complete recovery time and concentration of acid. Ordinates are times (minutes) required for recovery of complete transmissivity at 20°; abscissae are concentrations (volumes per cent of 1.42 HNO₃). The right hand curve represents the earlier (data of Table II), the left hand the later set of determinations.
Fig. 3 represents graphically the relation between the complete recovery time and the concentration of acid, as observed in the two sets of experiments just described. The curve approximates a straight line, indicating that the time is nearly proportional to the excess of concentration above a critical value (of about 53 to 54 per cent).

*Influence of Temperature on Recovery Process.*

Eight series of determinations in 65 per cent acid were made in the manner described at the temperature of about 3°C, the dish containing the acid being kept cool during the experiment by immersion in snow. The results are given in Table VI.

**TABLE VI.**

*Concentration of HNO₃, 65 Volumes Per Cent. Temperature 3°C.*

<table>
<thead>
<tr>
<th>Wire</th>
<th>Distance traveled.</th>
<th>Intervals since previous activation.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 min.</td>
<td>4 min.</td>
</tr>
<tr>
<td></td>
<td>cm.</td>
<td>cm.</td>
</tr>
<tr>
<td>A</td>
<td>4.1</td>
<td>4.9</td>
</tr>
<tr>
<td>B</td>
<td>3.8</td>
<td>5.8</td>
</tr>
<tr>
<td>C</td>
<td>4.9</td>
<td>9.0</td>
</tr>
<tr>
<td>D</td>
<td>2.2</td>
<td>3.3</td>
</tr>
<tr>
<td>E</td>
<td>1.7</td>
<td>5.5</td>
</tr>
<tr>
<td>F</td>
<td>3.1</td>
<td>3.9</td>
</tr>
<tr>
<td>G</td>
<td>3.5</td>
<td>3.9</td>
</tr>
<tr>
<td>H</td>
<td>5.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Average</td>
<td>3.5</td>
<td>5.2</td>
</tr>
</tbody>
</table>

It will be observed that recovery is four or five times slower at 3°C than at 20°C, only three cases out of eight showing full transmission after 16 minutes of recovery. There are also several other differences in the behavior of the wires at the two temperatures. The speed of transmission is several times slower at the low temperature; this retardation is perfectly distinct to the eye, but as yet no exact measurements of velocity have been made. The local reaction shows a less
vigorous effervescence and lasts for 5 or 6 seconds, as compared with about 1 second at 20°; i.e., the return to passivity is delayed in about the same proportion as the recovery of transmissivity. The disappearance of the deposit of dark oxide is also much more gradual. In partly recovered wires the retardation in the speed of the activation wave as it nears its stopping point is more distinct. There are also a larger number of apparently arbitrary irregularities in the distances traveled; thus Wires B and D transmitted for only about 8.5 cm. after 16 minutes in the acid, and other reversals in the expected order of the figures are seen in Wires A, C, E, F, and H. Apparently the conditions (irregular local circuits, etc.) which interfere with transmission are more effective when the local chemical processes are slower. The points representing the average transmissions at the several in-

![Graph showing rates of recovery in 65% acid at the two temperatures, 20° (Table V), and 3° (Table VI). Ordinates are distances (cm.), abscissae, times as before.](image-url)
ervals group themselves with fair regularity into a curve of the usual type but of more gradual slope (Fig. 4).

The characteristic temperature coefficient shown \((Q_{10} = 2 - 3)\) is evidently an expression of the dependence of repassivation and recovery of transmissivity upon chemical reactions occurring at the metallic surface. These reactions rebuild the surface film and restore it to its original condition. The temperature coefficients of the duration of the refractory period in cardiac and skeletal muscle and in nerve are closely similar. This resemblance may be regarded as a further confirmation of the view that in the latter case also the recovery of irritability and transmissivity is dependent primarily upon the chemical processes concerned in the restoration of the protoplasmic surface films.