

RESEMBLANCES BETWEEN THE ELECTROMOTOR VARIATIONS OF RHYTHMICALLY REACTING LIVING AND NON-LIVING SYSTEMS

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PLATES 1 AND 2

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It is well known that under certain conditions the reaction of iron wire with nitric acid exhibits an automatic rhythm of sometimes remarkable regularity, consisting in an alternation of active and passive periods.¹ In a recent study of this phenomenon² I have found the most regular rhythms in soft iron wire of low carbon content. Wire drawn from iron prepared by electrolysis of pure solutions of iron salts³ and the pure commercial soft iron known as Armco⁴ are especially favorable. In hard steel wire (piano wire) the tendency to rhythm is slight, and any rhythm shown is local and irregular. In general the essential conditions for a regular and rapid rhythm (*e.g.*, 50 to 100 per minute), involving all parts of a wire of some length (10 cm. and more), may be defined as follows: (1) The acid must be of sufficient strength (> 55 v.%,), such that the passive state is one of stable equilibrium; the wire then reverts automatically to the passive state after each activation (spontaneous repassivation); (2) the wire must transmit states of activation readily and quickly; (3) it must recover its transmissivity rapidly after activation; and (4)

¹ For a comprehensive account of rhythmical reactions in metals and in inorganic systems in general *cf.* the monograph by Kremann, R., "Die periodischen Erscheinungen in der Chemie," *Ahrens Sammlung chemischer und chemisch-technischer Vorträge*, 1913, 19, p. 289; also the recent book by Hedges and Myers, "The Problem of Physico-chemical Periodicity," London, E. Arnold & Co., 1926.

² Lillie, R. S., *Archivio di Scienze Biologiche*, 1928, 11, 102, and *Science*, 1928, 67, 593.

³ Kindly furnished by the U. S. Bureau of Standards, Washington.

⁴ American Rolling Mill Co. This iron contains 99.84% iron and less than 0.02% carbon, according to analyses furnished by the Company.

a single localized region must be present in which the reaction of the metal with the acid is continuous; this permanently active region may be compared with the nodal or pace-making region of the heart; it furnishes a constant activating influence to which the rest of the wire responds as soon as it has recovered sufficiently. From this controlling region waves of activation travel along the wire at intervals determined by the duration of the non-transmissive or "refractory" period which immediately follows each activation. In the rhythmically reacting wire, as in the heart, the regularity of the rhythm thus depends on the uniformity of the process of recovery, while the coordination or synchronization of activity in the different regions depends on transmission from a central or controlling region.

Since activation and transmission in passive iron are known to depend on the alteration or breakdown⁵ of the passivating surface film by local cathodic reduction, it is clear that the special properties of the film differ in different kinds of iron and are determined, in some manner not yet understood, by the special composition of the metallic surface. The film formed on steel wires during repassivation is highly resistant to reduction by the current of the local active-passive circuit; hence transmission of activation for more than a short distance is at first impossible. It is only after some minutes (in 70 v. % HNO_3 at 20°) that the wire regains the ability to transmit activation waves to an indefinite distance.⁶ On the other hand, in Armco wire and electrolytic wire, under precisely similar conditions, complete transmission returns within one second or less.² From evidence not yet published (having reference to the rates of recovery in different strengths of acid) it seems probable that the film formed on steel wire is at first relatively thick, and that recovery is the result of its progressive thinning by the solvent action of the acid, a certain limiting thickness (probably monomolecular) being eventually reached, corresponding to the final state of maximum transmissivity. In pure iron wire the passivating film is from the first thin; hence recovery is rapid. The influences of temperature and concentration of acid on the rate of recovery in Armco wire are similar in their general features

⁵ Theoretically, a sufficient interruption of continuity is all that is required.

⁶ Lillie, R. S., *J. Gen. Physiol.*, 1920, **3**, 107; 1925, **7**, 473.

to those found in steel wire, but the absolute rate of the process is much greater.

The rhythm is most readily demonstrated as follows. A short length of clean bright Armco wire (*e.g.*, 2 mm. thick, 1 to several cm. long) is placed in a flat-bottom vessel containing nitric acid of 60 to 80 v. % concentration.⁷ Usually a rhythmical reaction starts at once; the metallic surface shows at regular intervals an alternation between a steel bright and a dull lustre; on closer examination it is seen that the effervescence is confined to the dark periods, while during the bright periods the metal is non-reactive (passive). The number of cycles per minute varies usually between 40 and 100 or more, increasing with the concentration of acid and the temperature. The relative duration of the passive phase in each cycle increases with the strength of acid; in the weaker acid the appearance is that of a bright flash passing at intervals over the dark effervescent surface of the metal. If the acid be left unstirred, the rhythm soon becomes irregular and passes over into a continuous effervescence; but with stirring a regular rhythm may last indefinitely, *i.e.*, until most of the wire is dissolved.⁸

Experiment shows that under these conditions the presence of the continually active or controlling region depends on the contact of the metal with the glass. At some local area of contact the diffusion of reaction products and acid is retarded and the acid soon becomes too weak to repassivate the iron; the reaction then becomes continuous, *i.e.*, a permanently active or anodal area is established. A wire freely suspended in acid by thin glass filaments is non-rhythmical; when activated it shows a single reaction and immediately becomes again passive and remains so. Rhythm, however, can readily be induced by locally interfering with diffusion or otherwise maintaining a permanent local activity.⁹ The method finally adopted was to insert one end of the suspended wire into the interior of a narrow glass tube for a few millimeters. When such a wire is activated a few times (by touching

⁷ Volumes of HNO₃, C. P., Sp. Gr. 1.42, in 100 volumes of solution.

⁸ For further details *cf.* Lillie, R. S., *loc. cit.*²

⁹ *E.g.*, continual contact of copper, zinc or other metal, anodal in relation to passive iron, will induce rhythm; but such rhythms are irregular because of the difficulty of maintaining constant conditions.

with zinc) continuous effervescence soon appears in the enclosed region, and waves of activity then pass at regular intervals from this region along the whole wire. When the acid is stirred sufficiently to render the local conditions stationary, the rhythm preserves its regularity; otherwise it fluctuates and tends to accelerate. Withdrawing the wire from the tube or otherwise arresting activity in the the pace-making area (*e.g.*, by contact with platinum) at once arrests the rhythm, and the wire becomes permanently passive. Conversely, increasing the active area, as by inserting the wire farther into the tube, accelerates the rhythm.

The manner in which the rhythm is influenced by the extent of the controlling active area, temperature, concentration of acid, electrical polarization of the wire by an external current, and length of wire have been briefly described in the two papers already cited.^{9a} In the present paper the electromotor variations accompanying the rhythm will be described in some detail and their chief resemblances to the biological electromotor rhythms indicated. The variations of reaction velocity in the pulsating wire are an index of parallel variations in the passivating surface film, a regular rhythm implying alternate formation and breakdown of the film. The electrical variation is the most convenient and sensitive indicator of these changes in the film. Since there is evidence that variations in the semi-permeable protoplasmic surface films, affecting their permeability and electromotor properties, determine the bioelectric variations (membrane theory of Ostwald, Bernstein and their successors), the parallels between the electromotor variations in the two types of system are of interest as indicating the nature of the fundamental conditions determining activity in the irritable living system. In both cases the variations in chemical and electromotor activity appear to be primarily dependent on variations in the structure and composition of interfacial films.

The wire (Armco, *ca.* 2 mm. in diameter) was bent so that a straight portion of its length, *e.g.* 6 cm. long, could be immersed horizontally

^{9a} Another form of rhythmical action is seen in "circuit transmission" in which a single "trapped" activation wave travels continually round and round a circular wire immersed in 80 v. % HNO₃. Each region of such a wire shows a regular rhythm determined by the rate of travel of the wave. For a description of this phenomenon *cf.* R. S. Lillie, *Science*, 1929, 69, 305.

in the acid, which was contained in a vessel 10 cm. in diameter provided with an outflow tube inserted into its side 1.5 cm. above the bottom. The other end of the wire was attached to a key (Harvard cross circuit type) from which connection was made through a rheostat to the string galvanometer. The other electrode was a strip of platinum foil placed parallel to the wire at 2 to 3 cm. distance. A short portion of the wire, including the bend where it passed from the acid into the air, was coated with paraffin (to prevent irregular action which otherwise occurs at this region), leaving a length of *ca.* 5 cm. exposed to the acid. Opposite the free end of the wire was placed a glass tube, of calibre slightly greater than the diameter of the wire, into which the latter could be inserted for a short distance. In these experiments the inserted length was adjusted so as to secure the slowest rhythm that was stable under the conditions. The platinum electrode and the wire were connected with the terminals of a tube rheostat of low resistance (29 ohms), and wires led from the sliding contact and one terminal to the string galvanometer, a small instrument of the permanent magnet type. The tension of the string and the distance between slide and terminal of the rheostat were kept constant throughout the experiments. The speed of the recording surface was also constant at 0.8 cm. per second. The acid was led into the vessel by a siphon with its outlet near the insertion of the wire into the glass tube. The slow flow of acid provided the necessary stirring.

The records contained in the present paper were made at room temperature (20° to 22°). Under constant external conditions, with rhythms satisfactorily uniform, different wires show some variation in the rate of rhythm and in the form of the curve shown in each single cycle, but the essential features of the phenomenon are remarkably constant. The rate of rhythm increases with increase in the concentration of acid between 60 and 80 v.%. On either side of this range regular rhythms are difficult to obtain; at 55 v.% the automatic return of passivity is uncertain and irregular, while at 80 v.% and higher the tendency to passivity predominates and the active period becomes extremely brief. The rhythms at 80 v.% are typically rapid, broken and irregular (Fig. 1). At 85 v.% no satisfactory rhythms could be obtained.

In a large number of observations the rhythms observed in the

different concentrations of acid at 20–22° fell nearly always within the following ranges:

Concentration (v. % HNO ₃)	Rate per minute
60	30–40
65	45–60
70	60–80
75	85–100
80	120 or higher

An approach to a linear relation between rate and concentration seems indicated. The velocity and extent of the reaction in the pace-making area determine the rate at which iron ions pass into solution, and hence the intensity of the local activating current; and by the mass action law the reaction velocity should be proportional to the concentration of acid. But the area of the permanently active region cannot be controlled with any exactitude by the simple method used; it also varies as the reaction proceeds and the wire is dissolved away. There is also a rise of temperature in the enclosed column of acid, and this condition is probably largely responsible for the rapid acceleration of rhythm at the higher concentrations.

Of greater interest is the manner in which the form of the curve varies in the different solutions. Figs. 1 to 5 give typical examples of records obtained from short lengths of Armco wire under the conditions described. The concentrations of acid were respectively 80, 75, 70, 65 and 60 v.%. In these curves the upstroke corresponds to the change from passive to active, *i.e.*, the iron becomes more anodal. It is apparent that as the concentration falls the duration of the active phase increases; activity is also more readily maintained at a nearly constant level, *i.e.*, the tendency to passivity decreases. The plateau signifies a temporary maintenance of the active state; this feature of the curve becomes more pronounced with decrease in concentration. With still further decrease the active phase lengthens rapidly and becomes indefinitely prolonged at a concentration of *ca.* 55 v.%; *i.e.*, no spontaneous repassivation occurs in acid below this concentration. It is also noteworthy that the “dip” of the curve, representing the range of the variation of potential, is maximal at an intermediate concentration of 65 to 70 v.%. The period of steel-bright lustre is very brief in 60 v.% acid, as already mentioned, and the slightness of

the dip in this solution indicates that passivity is less completely attained than in stronger acid; this apparently signifies that the temporarily formed film covers a smaller portion of the surface.

In all cases the upstroke, signifying the breakdown of the passivating film, is rapid, reaching a maximum within a small fraction of a second. The process of repassivation, corresponding to the reformation of the film, then begins immediately, as indicated by the downward slope of the curve; this slope is steep and almost uniform in 80% acid and becomes more gradual as concentration decreases. The rather definite turning point or inflection in the downward slope, seen especially in the weaker acid, indicates that the passivation process undergoes rapid acceleration after reaching a certain critical stage. This stage may be taken as corresponding to the formation of a definite area of film-covered, *i.e.* cathodal, surface. Theoretical considerations indicate that as the cathodal area increases the total electric current between the active and the passive portions of the metallic surface also increases progressively up to a maximum;¹⁰ and it is probable

¹⁰ This current, other conditions being equal, would be maximal with equal areas of anode and cathode, since in general the strength of current in a battery system is directly proportional to the area of each electrode, *i.e.*, to the product of anodal and cathodal areas. If the area of the whole surface of the wire is unity, and if we regard anodal and cathodal areas as sharply defined, then if $\frac{1}{n}$ is the cathodal area, $\frac{n-1}{n}$ is the anodal area. The product of the two, $\frac{n-1}{n^2}$, is maximal when $n = 2$, *i.e.*, when the wire is half covered with the film.

It is probable, however, that the *density* (*i.e.*, intensity \div electrode area) of the local current traversing the surface of the wire, rather than its total intensity, is the chief factor to be considered, since the density determines the rate of electrochemical reduction or oxidation in each unit area of surface and hence the rate of the activating or passivating influence at the region concerned.

Designating the electrode areas as above, we see that over the cathodal surface the average current density is $\frac{n-1}{n^2} \div \frac{1}{n} = \frac{n-1}{n}$; over the anodal surface it is $\frac{n-1}{n^2} \div \frac{n-1}{n} = \frac{1}{n}$. That is, the average current density at any time over either electrode surface is directly proportional to the area of the other electrode surface. This shows, *e.g.*, that the density of the current at the cathodal (*i.e.* passive) surface increases linearly as the anodal surface increases, and *vice versa*. Activation

that the increase in the rate of passivation (*i.e.* of film formation over the previously active areas) corresponds to a critical increase in the intensity or density of this current. Anodal oxidation, recognized as a chief general means of inducing passivity in metals, is undoubtedly a main factor in the reformation of the passivating film.¹¹

In addition to these larger rhythmical variations of potential slight irregular fluctuations occur under a variety of conditions. In curves with well defined plateau (*e.g.* Figs. 4 and 5) a slight notch or dip is often seen just before the final rapid descent which accompanies repassivation. When the active phase is greatly prolonged, as in acid between 55 and 60 v. % concentration, an irregular rhythmical fluctuation often lasts throughout the entire active period. Similar variations frequently occur during the passive phase, especially when the "pause" is prolonged. Figs. 6 and 7 illustrate this condition. In the case illustrated by Fig. 6 the wire spontaneously ceased activity after a series of regular pulsations in 65 v. % acid (at 22°), apparently as a result of the dissolving away of the free end inside the glass tube. The last few beats show retardation with an accompanying increase in the range of variation; the potential then falls progressively, with irregular fluctuations indicating an oscillation between activating and passivating influences, to a level corresponding to complete passivity. In general, when the interval between successive cycles of a rhythmical series is prolonged, the variation of potential is increased;

requires more than a certain critical density of current; hence slightly scraping a passive wire in HNO₃ with glass may fail to activate the wire as a whole—*i.e.*, fail to cause a transmitted effect—while a larger scrape activates.⁶ Correspondingly, any local active area in a passive wire will spread, with an automatic acceleration (*i.e.* explosively), as soon as the area becomes large enough; similarly (although the conditions differ in detail) with a passive area. The steepness in both the ascent and descent of the curves may thus be understood. The irregular oscillations about a midway position shown in Figs. 6 and 7 are also probably an expression of the mutual influence exerted by local anodal and cathodal areas. The existence of such an influence between the active and passive areas of the same wire was early noted by Schönbein (*Philos. Mag.*, 1836, Vol. 9).

¹¹ This influence is seen (*e.g.*) in the retardation and arrest of the rhythm of a pulsating wire when it is made the anode of an external circuit.² The relative duration of the passive phase is at first lengthened, and with sufficient polarizing current the wire soon comes to rest in the passive state.

the form of the curve also undergoes a change which is illustrated in Figs. 6 and 7.

It will be seen from Fig. 6 that the whole variation of potential between activity and complete passivity in 60 v.‰ acid has approximately twice the range of that shown in each single cycle. The potential difference between completely active and completely passive wires, in 60 to 70 v.‰ HNO₃, as shown when the two are connected through a voltmeter, is of the order of 0.7 volt. During the rhythmical series the variation is *ca.* 0.35 volt, *i.e.*, the wire is reactivated before passivation has reached the complete or equilibrium stage. That this is the case is also shown by comparison with Fig. 8 which gives records of single variations resulting from successive brief contacts of zinc with a non-rhythmical wire in 65 v.‰ acid at intervals of a few seconds (22°). The variations are seen to be uniform in character and duration, but of approximately twice the range characteristic of each cycle of the rhythmical series.

In the comparison with living tissues the more general conditions are of chief interest and may be here briefly reviewed. The known relations between stimulation and variation of permeability indicate that alternate breakdown and reformation of interfacial films are the controlling factors in the living as well as in the non-living system, stimulation corresponding to breakdown of the protoplasmic surface film and recovery to its reformation. In both systems these processes are under electrical control. It is also to be noted that in general the recovery in living tissues is more directly associated with consumption of oxygen than is the stimulation; this would indicate that the normal semi-permeable properties of the film in the resting or recovered cell are determined by some oxidation product or products, or by some by-product of an oxidative reaction. Alternate oxidation and reduction are the essential features of the chemical reaction cycle in the passive iron system; and such general physiological facts as polar stimulation and electrotonus indicate that in this respect also the general conditions in irritable protoplasmic systems are similar. The complete dissimilarity in the chemical details of the controlling surface reactions in the two cases is in no sense incompatible with an identity in the fundamental physical conditions of the reactions.

The precise form of the electromotor curve in the rhythmical iron system shows considerable variation, as the foregoing examples illustrate. Similarly the form of the electrocardiogram varies widely in different animals;¹² these variations are to be referred in part to special anatomical peculiarities, as well as to differences in the time-relations and other features of the characteristic reaction cycles. In simple invertebrate hearts curves resembling closely those of the iron wires occur frequently. A rapid upstroke, sloping plateau and rapid downstroke are seen, for example, in the hearts of mollusca (*Aplysia*¹³) and Crustaceans (*Maja*,¹³ *Homarus*¹⁴). Oscillations in the plateau are a regular feature of the hearts of *Maja* and *Limulus*.¹³ In the vertebrate heart, with its several chambers and differentiation of conducting and contractile tissues, such resemblances are less evident, and variations in the position of the leading-off electrodes affect greatly the form of the curve. In many cases, however, the electromotor variation of a single chamber (*e.g.* ventricle) conforms to this type of curve.¹⁵

SUMMARY

1. The electromotor variations of pure iron wires, arranged to react rhythmically with nitric acid, are recorded and described.
2. Resemblances between these variations and those of rhythmically reacting living tissues (especially the heart) are pointed out and discussed.

EXPLANATION OF PLATES

PLATE 1

Figs. 1-5. Tracings from wires in HNO_3 of the concentrations 80, 75, 70, 65 and 60 v.%. Temperature 22°. The respective rates per minute are 140-150, 96-98, 60, 46 and 35.

¹² For a review *cf.* the article by W. Einthoven, *Handbuch der normalen und pathologischen Physiologie*, 1928, **8**, 785.

¹³ Hoffmann, P., *Archiv f. Anat. u. Physiol., Physiol. Abth.*, 1911, 135; *cf.* Fig. 14, Taf. X. *Cf.* also the tracings from the heart of *Helix* in the article of C. Lovatt Evans, *Zeitschr. Biol.*, 1912, **59**, 397, Fig. 3 and Plate VI, A, B, D.

¹⁴ Hogben, L., *Quart. J. Exper. Physiol.*, 1925, **15**, 264; *cf.* Figs. 21, 22.

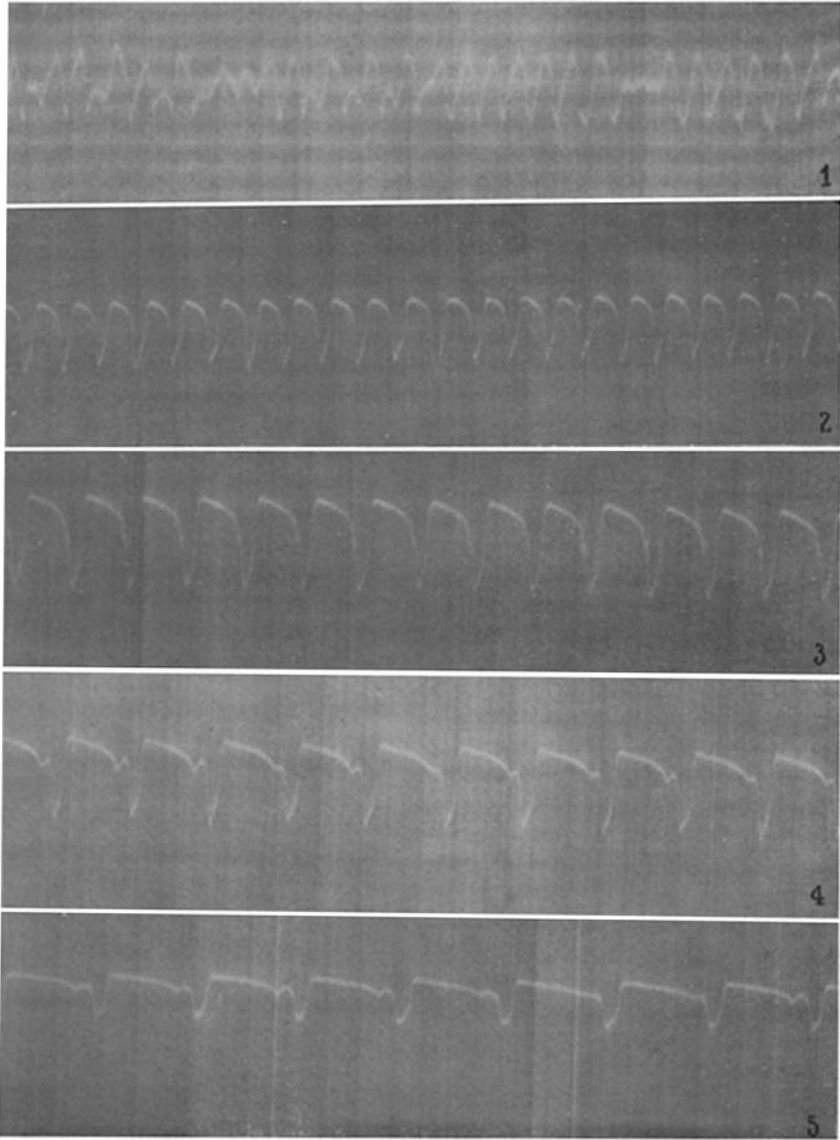
¹⁵ *Cf.* the tracings from the frog's heart in Einthoven's article,¹² pp. 813, 849.

PLATE 2

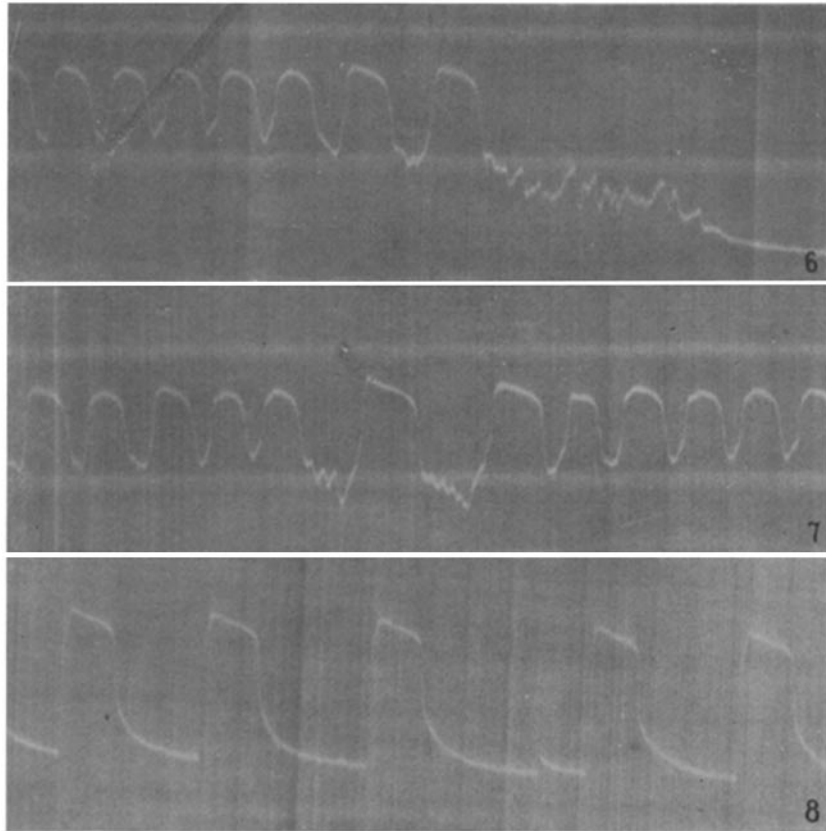
Fig. 6. Tracing from wire in 65 v.% HNO_3 showing relapse from rhythmical to permanently passive state at the end of a series of pulsations. Note rapid oscillations of potential during the relapse. Temperature $22^\circ\text{--}23^\circ$.

Fig. 7. Another part of the previous tracing showing prolonged pause with oscillations of potential between pulsations.

Fig. 8. Variations resulting from successive contacts of a non-rhythmical wire with zinc. HNO_3 65 v.%. Temperature 22° .



(Lillie: Resemblances between electromotor variations)



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