## XVI. NEUROPHYSIOLOGY*

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## A. HYDRATION OF BIOLOGICAL MACROMOLECULES

Nuclear magnetic resonance measurements at 60 mc on various partially dried tendon samples seem to confirm the structural relations of absorbed water with respect to the collagen molecules, as proposed in Quarterly Progress Report No. 56. When the water content is in the range of $25-50$ per cent of the dry weight (in an atmosphere of approximately 30-90 per cent relative humidity) the proton resonance signal shows three peaks in an oriented sample. The separation of the outer peaks follows approximately the relation ( $3 \cos ^{2} \epsilon-1$ ), where $\epsilon$ is the angle between the fiber direction and the magnetic field. This separation is the result of interaction of proton dipoles in the fiber direction; no sign has been found of interaction perpendicular to the fiber axis, as would be expected for water molecules that are restricted in motion over long correlation times by a hydrogen bond to one of the $C=O$ groups. The separation of interacting protons compares well with the length of the repeats (4.74A) in the fiber direction of the proposed hydration structure. The results indicate rapid reorientation of the individual water molecules, probably through saltatory reorientation of the type that accompanies Bjerrum defects in ice. When the water content is less than that necessary to maintain the simplest structure of the proposed kind along the collagen molecules ( 36 water mol ecules per 28.6 A repeat of one molecule, that is, 23 grams of water per 100 grams of dry collagen), the resonance curve does not show separate peaks, as is to be expected.
W. S. McCulloch, H. J. C. Berendsen

## B. LOGICALLY STABLE NETS

Nondegenerate logically stable nets compute an error-free output for simultaneous shifts in threshold of the component neurons. We consider nets of $\delta$ inputs to a rank of $\delta$ input neurons $\left(V_{i}\right)$ that excite a single output neuron $V_{o}$ that computes any required input-output function $\left[\mathrm{V}_{\mathrm{r}}\right]$. There are simple constructions for all $2^{2^{\delta}}\left[\mathrm{V}_{\mathrm{r}}\right]$ for the entire usable range of threshold, $\Delta \theta=2^{\delta}-2$. However, the Venn diagrams for some neurons are almost wholly filled with jots, whereas others are almost empty.

In dealing with the death of cells, individual fluctuations of threshold, and possible

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Fig. XVI-1. The only two exceptions to the rule for maximum range in threshold of logically stable nets. Numbers give the order in which jots appear.
(a) $\delta=2, \gamma=2^{\delta-1}, \Delta \theta_{\text {max }}=2 / 4=50$ per cent.
(b) $\delta=4, \gamma=2^{\delta-1}, \Delta \theta_{\max }=12 / 16=75$ per cent.
destruction of cell fibers, it is found that all neurons must have approximately the same açtivity in order to decrease appreciably the probability of error in the output. Hence we seek the rules for the construction of nets with the same number of jots in $\mathrm{V}_{\mathrm{o}}$ and in each Venn of $\mathrm{V}_{\mathrm{i}}$ and with a maximum range in threshold $(\Delta \theta)$ for each neuron. For this, two useful concepts are those of the complement (C) and the dual (D), where C is the negate of a Venn function and D is a disjunct of the product of the complements of the component propositions of the jots. Thus, if $\left(\mathrm{V}_{\mathrm{i}}\right) \mathrm{V}_{\mathrm{o}}=\left[\mathrm{V}_{\mathrm{r}}\right]$, then $\left(\mathrm{V}_{\mathrm{i}}\right) \mathrm{CV} \mathrm{V}_{\mathrm{o}}=\left[\mathrm{CV} \mathrm{V}_{\mathrm{r}}\right]$, $\left(\mathrm{DV}_{\mathrm{i}}\right) \mathrm{V}_{\mathrm{o}}=\left[\mathrm{DV}_{\mathrm{r}}\right]$, and $\left(\mathrm{CV}_{\mathrm{i}}\right) \mathrm{DV}_{\mathrm{o}}=\left[\mathrm{V}_{\mathrm{r}}\right]$, yielding $\left(\mathrm{CDV}_{\mathrm{i}}\right) \mathrm{CDV}_{\mathrm{o}}=\left[\mathrm{CDV}_{\mathrm{r}}\right]$. The last expression transforms a logically stable net, which computes a $\gamma$-jot function $\left[\mathrm{V}_{\mathrm{r}}\right]$ into one that computes a $\left(2^{\delta}-\gamma\right)$-jot function $\left[V_{r}\right]$.

Finally, let $P$ be any specific permutation of the jots in a Venn; then $\left(P_{i}\right) V_{o}=$ $\left[\mathrm{PV}_{\mathrm{r}}\right]$. This transforms any net with a $\gamma$-jot function [ $\mathrm{V}_{\mathrm{r}}$ ] into any other net with a $\gamma$-jot function $\left[\mathrm{V}_{\mathrm{r}}\right]$. Hence only $2^{\delta-1}+1$ out of $2^{2^{\delta}}$ nets need be investigated.

Let x be the number of jots in $\mathrm{V}_{\mathrm{i}}$ and $\mathrm{V}_{\mathrm{o}}$ at highest threshold and let y be the number of empty spaces in $V_{i}$ and $V_{o}$ at the lowest threshold for which the net computes a zeroerror output. If $\mathrm{i}-\mathrm{l}<\mathrm{a} \leqslant \mathrm{i}$, then define $\langle\mathrm{a}\rangle=\mathrm{i}$. The maximum range in threshold is $\Delta \theta=2^{\delta}-\mathrm{x}-\mathrm{y}$ with $\mathrm{y}=\langle\gamma / \delta\rangle$ and $\mathrm{x}=\max \left(\langle\sqrt{\gamma}\rangle,\left\langle\frac{\gamma}{\delta}\right\rangle\right)$, except when $\gamma=\delta^{2}-1$, in which case $x=\delta+1$. There are only two exceptions to this rule for which a higher $\Delta \theta$ can be obtained. These are given in Fig. XVI-I.

The range of threshold is smallest when $\gamma=2^{\delta-1}$. In this case, $\Delta \theta=2^{\delta}[1-(1 / \delta)]$. Thus even under extremely poor conditions, a very large range in threshold is obtainable.
W. S. McCulloch, M. Blum

## C. MANY-VALUED LOGICS AND NEURONAL NETS

An investigation concerning the usefulness of many-valued logics in the construction of neuronal models has been carried out. A universal element for modal logic (1) has been found, which, in terms of a threshold neuron representation,
(a) fires spontaneously and maximally for no inputs
(b) does not fire for all inputs
(c) is an almost linear antimonotone function of its inputs.

This element makes possible the synthesis of neuronal nets corresponding to modal logical functions. All such nets are, almost everywhere, order-continuous functions of their inputs (2).

An attempt was made, using these nets, to improve upon von Neumann's solution to the problem of obtaining reliable nets consisting of unreliable components (3). Although no positive results were obtained using modal logical nets, the investigation has led to a consideration of Brandt groupoids (4) as a means of obtaining an improvement on von Neumann's result.
J. D. Cowan

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## D. NOTE ON DEATHS AND FITS OF FORMAL NEURONS

A formal neuron is said to be dead if its normal response to input pulses is altered in such a way that it will never again fire. A formal neuron is said to have a fit if its normal response to input pulses is altered so that it keeps on firing, regardless of its input.

Neuronal nets in which the neurons are susceptible to deaths and fits can be constructed in such a way that the input-output relation of the net is not disturbed by deaths and fits of some of the neurons.

Figure XVI-2 gives an example of a net in which one of the neurons in the input layer ( $\mathrm{V}_{\mathrm{i}}$ layer) may be dead and one may have a fit without disturbing the relation
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Fig. XVI-2. Sample net of neurons, each having three inputs, and Venn diagrams defining the function of the net.
between the input ( $\mathrm{A}, \mathrm{B}, \mathrm{C}$ ) and the output D. Figure XVI-2a shows the construction of the net; Fig. XVI-2b shows the computation with all neurons of $\mathrm{V}_{\mathrm{i}}$ working correctly; and Fig. XVI-2c shows the computation with one neuron dead, one having a fit, and one working correctly.

A majority organ (1) is defined as a neuron whose Venn diagram has jots in the $2^{\delta-1}$ of its $2^{\delta}$ spaces that correspond to $(\delta+1) / 2$ or more simultaneous active inputs, and zeros in the remaining $2^{\delta-1}$ spaces.

The majority organ (or its complement) is the most powerful neuron with respect to deaths and fits. If an infallible majority organ $V_{o}$ receives its input from a $V_{i}$ layer of $\delta$ neurons, which are susceptible to deaths and fits, it preserves the input-output relation of the net if there are, at most, $(\delta-1) / 2$ deaths and $(\delta-1) / 2$ fits of neurons in the $V_{i}$ layer.

If $\delta$ is odd, such a net is symmetrically equipped against deaths and fits because $(\delta-1) / 2$ is an integer. If $\delta$ is even, the majority organ $V_{o}$ can be such that it withstands, at most, $\delta / 2$ deaths and $\delta / 2-1$ fits, or such that it withstands, at most, $\delta / 2-1$ deaths and $\delta / 2$ fits in the $V_{i}$ layer. Here, we assume that $\delta$ is odd.


Fig. XVI-3. Probability $a_{\delta}(p)$ of erroneous output as a function of the probability $p$ of error in the component input neurons, each having $\delta$ inputs.

The output of any given correctly working neuronal net fires if and only if its input belongs to a subclass of the totality of its possible input configurations; this subclass depends only on the net, that is, on the neurons and their interconnections. If a member of this subclass is presented, we say "the world is that case" (or, one of those cases); if not, we say "the world is not that case." In Fig. XVI-2, for instance, the world is that case for $\mathrm{A} . \mathrm{B} \sim \mathrm{C}, \sim \mathrm{A} . \mathrm{B} . \mathrm{C}$, and $\sim \mathrm{A} . \mathrm{B} \sim \mathrm{C}$.

We assign to each fallible neuron a probability $p$ of being dead, a probability $p$ of having a fit, and hence a probability $1-2 p$ of working correctly. It is clear that $0 \leqslant p \leqslant 0.5$.

If we consider a single fallible neuron and if the world is that case, then the error probability $P_{w}$ is equal to $p$; $p$ being the probability that the neuron is dead, and therefore not firing, even though the world is that case. If the world is not that case, the error probability $P_{n w}$ is equal to $p ; p$ being the probability that the neuron has a fit. These errors are mutually exclusive, and thus the error probability is

$$
P_{e}=\sigma P_{W}+(1-\sigma) P_{n W}=p
$$

where $\sigma$ is the probability of the world's being that case.
Consider a net with a $V_{i}$ layer of $\delta$ fallible neurons connected to one infallible majority organ (see, for example, Fig. XVI-2a). If the world is that case, this net errs only if $(\delta+1) / 2$ or more neurons in the $V_{i}$ layer are dead. (The remainder are either functioning correctly or having a fit.) The error probability can be calculated by tabulating all possibilities of error with their associated probabilities, and adding these probabilities. We find $P_{W}=a_{\delta}(\mathrm{p})$, where $a$ is a function of p and has $\delta$ as a parameter.

If the world is not that case, the net errs only if $(\delta+1) / 2$ or more neurons have a fit. By tabulating all possibilities, we find that $\mathrm{P}_{\mathrm{nw}}=a_{\delta}(\mathrm{p})$. Because deaths and fits are

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interchanged, it is obvious that $P_{w}=P_{n w}$, and that the errors are mutually exclusive. Thus the error probability of the net is

$$
\mathrm{P}_{\mathrm{e}}(0)=\sigma \mathrm{P}_{\mathrm{w}}+(1-\sigma) \mathrm{P}_{\mathrm{nw}}=a
$$

The symbol $a$ is used as shorthand for $a_{\delta}(p)$, and $P_{e}(n)$ is the error probability of a net with $n$ layers of majority organs between $\mathrm{V}_{\mathrm{i}}$ and $\mathrm{V}_{\mathrm{n}} ; a$ is calculated for $\delta=3, \delta=5$, and $\delta=7$. The results are plotted in Fig. XVI-3. It is clear that $a=p$ for $p=0$. and $\mathrm{p}=0.5$. Figure XVI-3 shows that $a<p$ for $0<p<0.5$.

We can conclude that the use of a $V_{i}$ layer that is working on an infallible majority organ $V_{o}$, instead of a single $V_{i}$ neuron, results in improvement as far as resistance to deaths and fits of neurons is concerned.

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## E. FORM-FUNCTION RELATIONS IN THE RETINA

From Ramon y Cajal's essay on the frog retina, a rare treatise published in 1894, it quickly became clear that we could decipher the shapes of cells by treating them as pictographs whose meanings were the operations on the visual image we had found in the frog's optic nerve. This could be done without any recourse to such notions as facilitation, inhibition, and so on. This approach is introduced in a paper to be published in the Proceedings of the International Symposium on Principles of Sensory Communication, 1959, edited by W. A. Rosenblith, and we hope to develop it further. H. R. Maturana is checking some of the more subtle anatomical questions brought up by Ramon y Cajal. He will continue this work in Chile and will supply some much-needed emendations. Briefly, it appears that there are strong reasons to suppose that the outer part of the inner plexiform layer in frog retina is concerned with some function(s) of average light intensity or changes thereof at the receptors, whereas the inner part is concerned with local boundaries in the image on the receptors. Two of the operations we have described in the optic nerve - the boundary detectors, and the dimming detectors - can be ascribed on many grounds to cells that in the first case are connected only to the inner layer, and in the second, only to the outer layer. The other two operations, convexity detection and moving-edge (or changing-contrast) detection are combinations of both layers, but in two different dendritic patterns. The first pattern (E) is


Fig. XVI-4. Dendrite distribution.
connected to both layers in such a way that every small process sees a combination of both layers for a very small subarea, and there are many such processes. The second (H) is made by a few large dendrites, each of which is connected widely in both layers. This difference is conveyed by Fig. XVI-4.

A full description of the anatomy and the arguments relating form to function would be much too long to give here.
J. Y. Lettvin and H. R. Maturana

## F. HEARING SENSES IN THE FROG

F. S. Axelrod, an undergraduate working with our group on his thesis, has found some interesting units in the eighth nerve of the frog. There are three sorts, so far, to which he has paid special attention. The first is a curious auditory element. It responds to frequencies in the $600-700 \mathrm{cps}$ band, but adapts very rapidly so that there is very little response, except initially, to the turning on of a sine wave of constant amplitude in that band. If a transient having components in that band is presented, the fiber follows the repetition rate of that transient quite faithfully up to approximately 100 cps , then breaks into submultiples of higher repetition rates. This fiber has the amusing property that it responds very well and with very low threshold to the sound "ah" no matter who says it, at whatever pitch he says it, and even if he whispers it but it will not respond to the sound "ee" at all. (A phoneme filter!) This, of course, is

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what one would expect, knowing the nature of formants, but it is quite a striking phe nomenon. The second type seems to be a conventional auditory fiber, looking very much like those described by N. Y-S. Kiang for the cat. There is a spontaneous rate in silence that increases slightly with low-frequency sound, then becomes locked with that sound, and then increases further, as the frequency is increased, until a certain critical point is reached. Above that critical frequency, sound not only produces no response but inhibits the spontaneous activity. The third type, Axelrod has called "seismic detectors" (1). They are extremely sensitive to vibrations transmitted through the ground to the animal but are not sensitive to air-borne sound. They detect even the faintest footfalls in the laboratory, and Axelrod has used them to count passing trucks. These detectors most probably have their origin in the part of the vestibular system wherein the receptors are attached to a flap that projects out more or less parallel to the ground. This has ordinarily been thought to be a gravity detector, but is also obviously suited for an accelerometer (1).

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References

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## G. OPTIC-NERVE FUNCTIONS IN THE RAT

R. M. Burde, an undergraduate who is working on the optic nerve of the rat, has obtained some very disquieting results. The size of receptive field of an optic nerve fiber in the rat and the operation on the image done by that fiber depend on whether or not the animal is anesthetized, is asleep or awake, is attending to or uninterested in the stimulus. There are several types of these fibers, and they do not seem to be very much like those that have been described in studies on the cat. It has been suspected for quite a while that there is a strong efferent control on retinal function in mammals. Indeed, the results of R. Hernandez-Peón, of the Departmerit of Medical Physiology, University of Mexico, on changes in optic-nerve transient responses (both in man and in cat) to repeated visual stimuli but with differences of degree of interest are well known; and Lucia R. Ronchi and her group in Florence have shown that the electroretinogram of a man can be evoked by a click that has been associated with light flashes. One might certainly have expected differences in sensitivity of receptive fields with differences in consciousness or attention. But Burde seems to think that it is not so much the sensitivity as the actual operation on the visual image that changes. That would make the whole problem of investigating the mammalian retina extremely difficult indeed.

J. Y. Lettvin and H. R. Maturana

## H. OLFACTORY SENSE IN AMPHIBIA AND REPTILIA

We are still working on olfaction. We had encouraging results with two land -phase Ambystomata tigrina tigrina - that is, we recorded single-fiber activity - but we cannot obtain any more of this species until April 1960, when the animals make the transition from water phase to land phase. Meanwhile, we have explored the comparative anatomy of the olfactory nerves in vertebrates, and have come to a number of conclusions: (a) No mammal is suitable for making direct recording from single olfactory fibers, by reason of the relations of the nerve to the entorhinal mucosa, the cribriform plate, and the olfactory bulb. These relations are such that, although delicate surgery may expose a bundle, it is unlikely that the bundle would survive the operation. The splitting of the nerve into many small filaments held by the cribriform plate makes it almost impossible to work close to the bulb. (b) Of the lower forms, the batrachians have poorly developed olfactory nerves, as well as a cartilaginous porifer enveloping the dispersed fila olfactoria in passage through the fenestra olfactoria - roughly the same situation as with the cribriform plate of mammals. (c) Certain other amphibia are anatomically suitable; for example, the Gymnophiona, which are not obtainable here, and a few salamanders, as well as the A. tigrinum tigrinum. (d) Most promising, however, seem certain reptilia whose nerve is large, long, well-developed, and compact. This class includes the almost legendary Sphenodon, the gecko, the Lacertidae (but not Iguanidae), certain snakes, and particularly the Crocodilia.

We have succeeded in recording olfactory activity in the primary fibers of nerve I in Alligator mississipiensis (gray), using the electrodes that were employed in the previous studies made by Lettvin and Maturana on the optic nerve. The spikes are of comparable height and shape to the unmyelinated fiber spikes that they found. It is possible to record from a single fiber for as long as desired, and when several fibers are picked up simultaneously they can be differentiated by amplitude. Different fibers respond preferentially to different groups of olfactory stimuli. (Alligators appear to like skatole and dislike benzaldehyde, l-octanol and ethyl-acetate.) It is possible in many instances to record from one particular fiber, move the electrode away, and then return to the original one again.

Our electrodes are inserted through the medial cartilaginous wall of the orbit. The eye is enucleated under $\mathrm{CO}_{2}$ anesthesia, and the alligator is allowed to come out of the anesthetic before any attempt is made to record.

We have succeeded in assembling the necessary apparatus and supplies to make an electrode that is capable of smelling, as mentioned in Quarterly Progress Report No. 56. That is, we have been able to use the great sensitivity to "poisoning" of certain electrochemical systems in constructing an artificial olfactory receptor with a controlled spectrum of sensitivities. A few weeks ago, we should have expounded

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upon the theoretical basis of this program at some length; but recently we have become more and more dubious of the so-called "semi-empirical" treatment of localized electrons in conjugated organic molecules, particularly in its application to kinetic analysis; and therefore we shall not give any implied approval to the usual molecular orbital treatments and formal reaction-rate theory by publishing speculations that presuppose the substantial validity of that treatment. Not doubting, however, that graphite is a conductor, and that the cyanines and merocyanines are dyes, we are pursuing our experimental program in spite of reservations about quantum chemistry.

R. C. Gesteland and W. H. Pitts

## I. DEVICES FOR USE IN BIOLOGICAL MEASUREMENTS

Several devices have been developed for our work, and we describe a few of them here. For example, a set of devices that was originally worked on by S. J. Wiesner during the past summer is now being used in modified form by J. H. Rekosh. The argument used by Wiesner was this: Suppose that a set of photoresistors were so arranged in layers that all of the layers had the same properties with respect to the variation of resistance with light and all were semitransparent, so that each absorbed a fixed fraction of the light incident to it. The transmission of the light through the sandwich would be exponentially attenuated with depth. Now, suppose that each layer is connected to a current source. Then, the total current through the sandwich must be proportional to the logarithm of the light intensity hitting the sandwich because each layer - since it is connected to a current source - is in effect a saturable element, and successive layers become saturated at successive equal multiples of the light intensity.

However, building such a sandwich is difficult; it is easier, as Wiesner showed, to take a set of matched photoresistors, then to lay a single film of a standard grey over the first photoresistor, two films over the second, three films over the third, and so on, and to connect all of the photoresistors through separate resistors to the same volt age source. The total current through that voltage source is logarithmic with respect to light intensity, as one would expect.

But a third mode also can be used. Silicon diodes are said to have a V=log I charac teristic in the forward direction. Rekosh uses the SG22, the so-called Stabistor (Transitron), a voltage reference Zener diode. Here, of course, a photoresistor in series with the SG22 gives an elegant measure of the logarithm of light intensity over a wide range. It occurred to Rekosh that if four such units were made and each pair were fed into each pair of plates of an oscilloscope with push-pull input and high rejection ratio for inphase signal, then, if one pair had a red filter pitted against a green filter, the other a blue against yellow, the position of the oscilloscope spot should measure color on a color quadrangle. Saturation would be indicated by distance from the center, and color
indicated by the angle, and this measure ought to be little affected by the total average intensity if all units were supplied by a common current source.

In using glass micropipettes filled with electrolyte we noticed, as certainly others must have done, that the resistance through the pipette varies markedly with bending. Because the pipettes are approximately $2 / 3 \mathrm{mil}$ in diameter at the shank, tapering to $1 / 50 \mathrm{mil}$ at the tip, and are made of glass, they not only bend easily but are perfectly elastic. It occurred to J. del Castillo, University of Puerto Rico, and to us that such probes make good miniature strain gauges. We used a micropipette in a single muscle fiber and, impressing across it alternating current from an almost pure current source and balancing out that signal with a virtual bridge, we were able to record simultaneously the fluctuations in membrane potential in the fiber and the mechanical contraction.

Measuring blood pressure external to an artery gives values that are different from those recorded within the artery. One of the problems brought to us by clinicians is that of measuring accurately the diastolic pressure. It struck us that the difficulty is easily resolved by the following scheme. The electric signal of the heart precedes the pulse wave by a significant amount. The largest transient of the EKG, that is, the QRS, can be used to start an interval-measuring device that is stopped by the first inflection of the pulse wave. If a pressure cuff is placed on the arm and the pulse wave beyond the cuff is measured, then, when the cuff is inflated and exceeds the diastolic pressure, the first inflection will be further delayed, for inflating the cuff is equivalent to putting a center cutoff on the pulse wave. Thus, the diastolic pressure can be said to be the pressure of the cuff at which the interval between the QRS and the first inflection of the pulse wave beyond the cuff begins to increase. This is both a more delicate and more reliable measure than those used before. The systolic pressure, of course, is the cuff pressure at which the pulse wave disappears beyond the cuff. This device for measuring diastolic pressure is trivially easy to build.

J. Y. Lettvin

## J. ELECTROCHEMILUMINESCENCE

Certain substances are noted for showing a brilliant chemiluminescence when oxidized in solution under the proper conditions. Best known among these are "luminol" (5-amino-(1,2) dihydrophthalazinedione) and "lucigenin" (dimethyl (9, 9') bis acridinium nitrate). Usually the luminescence is produced by mixing an alkaline solution of the substance with $\mathrm{H}_{2} \mathrm{O}_{2}$ and then adding a catalyst - for example, ferrocyanide, hypochlorite, traces of heavy metals - whereupon, a bright glow then appears throughout the solution. With different catalysts, different intensities of light appear, but the duration seems inversely proportional to the brightness. The explanations in the literature of this phenomenon seemed to us rather unsatisfactory. In particular, no reason
is given for the fact that the luminescence is confined to a few compounds of apparently quite unrelated structures. We therefore decided to see whether the luminescence could be evoked without a catalyst at the surface of a passive electrode that was polarized to a suitable anodic potential. If so, the powerful methods of electrochemical kinetics could be used to investigate the mechanism. We began with luminol, which is readily available, and the following remarks refer to it.

The experiment succeeded at once. When two electrodes of smooth platinum foil were immersed in an alkaline solution of luminol, and a voltage was applied, a visible glow appeared over the entire anode. This glow began at a potential difference of approximately 1 volt (this was below that necessary for visible evolution of oxygen) and it increased brightness with voltage even through the range in which $\mathrm{O}_{2}$ was rapidly evolved. When $\mathrm{H}_{2} \mathrm{O}_{2}$ (but no catalyst) was added to the solution, the glow became very bright, almost as much as an equal area of fireflies' tails and at least as great as that producible by any catalyst in solution, but without any significant luminescence except at the electrode. Moreover, the brightness, especially at high current densities, appears to be controlled by diffusion; it is brightest at the edges of the foil, shows a transient maximum when the current is switched on, and increases markedly when the solution is stirred. At this point, F. Frazier, a high-school student, became interested in the question and, with our advice, started to make almost systematic experiments in which the geometry of the electrode was simplified enough to make it possible to interpret the current-voltage relationships, that is, the differential ac impedance (of the cell to a small ac signal superimposed upon a slowly varying voltage), as well as the total current, which is the usual polarogram. He used a proper reference electrode and suitable measuring apparatus, and he made a concurrent direct measurement of the light produced and its relation to the electrochemical state of the system. Naturally, one must examine all of these in relation to the relevant chemical parameters.
B. Howland, of Lincoln Laboratory, M.I.T., has recently designed an appropriate measuring system for the luminescence, and in making some preliminary observations he has discovered a number of new facts that seem to indicate promising technical applications. First, even without systematically determining the best possible composition of the solution, he found it very easy (if the dc potential between two electrodes is properly adjusted) to make the light emitted follow a superimposed ac signal to 5 kc , at least, and perhaps even higher. Secondly, he discovered that, with certain proportions of the reactants and a fairly high potential across the cell, the glow would quickly diminish to an almost imperceptible level and remain there; but when the electrode was moved, or a system of fluid currents was set up near the electrode in the solution, the glow would reappear with great brilliance and remain until the internal motion of the solution had subsided. This effect is much less marked at lower potential differences, as one would expect if it proceeded from an almost complete depletion of one of the
reactants in the boundary layer surrounding the anode. It seems more marked with gold anodes than with platinum. The response to fluid motion can be varied substantially by varying the voltage, which seems possible over a wider range with gold than with platinum, since oxygen is not evolved - a fact that is consonant with the higher oxygen overvoltage of gold. We should mention that these effects are likewise present with other passive electrodes, for example, stainless steel, but the quantitative behavior is naturally different. Strangely enough, a platinized platinum electrode emits no light at any voltage, and no light can be produced at any cathode, even with a solution saturated with oxygen.

Howland believes that these phenomena, when the best conditions are discovered, may have two sorts of applications. The first would be for computer read outs, where the advantage over existing systems lies in the low voltages ( 1.00 volts to 1.5 or 2 volts) that are necessary to produce a reasonably bright light at small current. The second would lie in the field of hydrodynamic and aerodynamic modeling, particularly when quantities such as the distribution of heat flux across the surface of an object placed in a complicated field of motion are to be measured; because heat transfer obeys laws that are mathematically similar to those governing diffusion, the intensity of the light emitted by a point of a model, used as an electrode and placed in a similar field of fluid motion, would represent the quantity desired and could be observed simply by taking photographs. (We should remark that the light emitted is greenish-blue, and therefore strongly actinic.)

We must emphasize that everything said here is purely tentative at present and is subject to revision when our measurements are finished with more scrupulously purified solutions and better defined electrochemical conditions. We mean also to investigate, at least roughly, the corresponding phenornena for a few other chemiluminescent systems (notably lucigenin, which, in bulk, is said to yield 100 times the brightness obtainable from luminol, but must be synthesized by rather tedious and unsatisfactory methods, perhaps on dibenzanthrone).

A convenient starting solution for observing these effects consists of 30 mg luminol, 4 ml 3 per cent $\mathrm{H}_{2} \mathrm{O}_{2}, 100 \mathrm{ml} \mathrm{H}, \mathrm{O}$, and 1 ml 2 N NaOH . This solution operates over a wide range of voltages. It is quite possible that more effective compositions exist; how ever, this solution displays the effects mentioned in the discussion of possible applications.
R. C. Gesteland, B. Howland, W. H. Pitts


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