Propagation of Chemical Reactions in Space

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Translators' Note
This article is an English translation of a paper by Robert Luther on his discovery, investigation, and analysis of chemical waves. The source of the translation is a transcript of a lecture and the following discussion at the Main Meeting of the Deutsche Bunsengesellschaft fur Angewandte Physikalische Chemie held in Dresden, Germany, from May 21 to 24, 1906. It was published by Luther in Z. fur Elektrochemie 1906, 12(32), 596. A discussion of this article is presented in the next paper in this issue (page 742).

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Session on Tuesday, May 22, 9:00 a.m. in the Main Auditorium of the Chemistry Laboratory of the Polytechnic Institute
It is known that a stimulus received on a nerve ending propagates through the nerve with a certain finite and not excessively large velocity of about 50 m/s. The mode of this propagation has not been elucidated so far. However, there has not been a lack of experiments that attempted to provide a clarification or, at least, to establish a plausible picture of the processes in the nerve on the basis of known phenomena. Most often electrical devices were used for that purpose: for example, parallel or sequentially connected self-inductances and capacitances. Yet I want to focus on nonelectrical hypotheses in which the generation of different electrical potentials is a subordinate phenomenon. As far as I know, it was the late “Universalgelehrte” Herbert Spencer who first pointed to the analogy between the propagation of a stimulus in the nerve and the propagating transformation of a solid from a metastable into a stable form. Later Ostwald used the initiation and propagation of crystallization in a supercooled melt as an example. This phenomenon is well known: if, for example, a piece of glass tubing that contains a supercooled melt of thiosulfate is inoculated at one end with a trace of solid thiosulfate, the crystallization will gradually propagate through the tube. However, nerves are solid structures neither before nor after stimulation and the question arises whether a similar propagation is also possible in liquid homogeneous systems.

Several years ago Herr Schilow and myself discussed this possibility. We also performed some preliminary experiments. I would like to show you now one such experiment. Herr cand. Meinecke helped with the preparation of the experiment. (Demonstration.)

The velocity of propagation is small, only a few centimeters per hour. Based on theory, this is to be expected. In principle, however, there is nothing to prevent any large velocity since the velocity of propagation (V) is given by

\[ V = a(D - C) \]

where \( a \) is a numeric factor, \( D \) a diffusion coefficient, \( C \) a concentration, and \( K \) a rate constant. When \( K \) increases sufficiently, so does the velocity of propagation.

While the border between red and white is moving slowly, I would like to give some further explanation. In studying the actual cause of the propagation of crystallizations, one soon arrives at the conclusion that the processes that propagate in a homogeneous medium have to be autocatalytic.

Let us choose as an example the autocatalytic decomposition of the salts of alkyl sulfonic acids. Suppose a tube is filled with a solution of methyl or ethyl sulfate. To prevent convection, the solution is to be gelled.

The neutral alkyl sulfates are very stable in aqueous solution but slowly give off sulfuric acid upon acidification. If I introduce some acid on one end of the tube then, under the catalytic influence of \( H^+ \), hydrolysis ensues and new \( H^+ \) ions are formed. These ions diffuse to the right and cause the formation of more acid. In this way, the decomposition slowly moves through the tube.

The selection of useful reactions is not large at the moment, for we do not know too many autocatalytic processes. In addition, the reaction has to be linked to a color change in order to observe the propagation with the naked eye.

In the chosen example of a salt of ethyl sulfate, one can use any indicator, such as litmus, whose color change will show the movement of the \( \text{H}^+ \)-ion front. A different example is a reaction studied by Eckstadt that involves nitric acid and hydroiodic acid. Nitrous acid or NO functions as the initiat-

\[ \text{Equation of the following solutions were mixed:} \]

A. 1/12 mole \( \text{H}_2\text{SO}_4 \) + 1/12 mole \( \text{C}_2\text{O}_4\text{H}_2 \) (oxalic acid) per liter. B. 1/125 mole \( \text{KMnO}_4 \) per liter.

If reducing substances are excluded during the preparation of the solutions, the mixture may be kept unchanged for more than 30 min at room temperature. After that time, decolorization sets in rather rapidly. The freshly prepared mixture was transferred to a well sterilized oval test tube. Some drops of the already reacted mixture were cautiously added to the top of the solution. The borderline between the lower (red) liquid and the upper (colorless) liquid was marked with a wire ring that was pushed over the tube. The test tube was projected, whereby the gradual movement of the interface of the color into the red region could be demonstrated.

1 Equal volumes of the following solutions were mixed:
A. 1/12 mole \( \text{H}_2\text{SO}_4 \) + 1/12 mole \( \text{C}_2\text{O}_4\text{H}_2 \) (oxalic acid) per liter. B. 1/125 mole \( \text{KMnO}_4 \) per liter.
through reaction with nitric acid, produces again HNO₃, and so on.

Another example is the autocatalytic reduction of permanganate. In particular the reaction scheme with oxalic acid was largely clarified through the investigations of Harcourt and Esson, and Schilow and Skrabal. During the reaction Mn²⁺ is produced which—as was first discovered by Hempel—accelerates the reduction of permanganate and thus causes the propagation. The reaction between KMnO₄ and oxalic acid was chosen for the demonstration.

Finally the autocatalytic reductions of halogen acids of type HXO₃ provide good examples. Bromic acid in particular has been studied by Schilow. Bromic acid in weakly acidic solution is sluggish toward many reducing agents, for example arsenous acid. In contrast, bromic acid reacts rapidly with bromide ion, apparently following the generally applicable scheme (1):

\[
\text{HBrO₃} + \text{HBr} = \text{HBrO₂} + \text{HBrO}. \\
\text{resp.} \text{BrO₂} + 1/2 \text{Br}_2 + \text{H}_2\text{O}
\]

As soon as one adds a trace of bromide to the acidified mixture of bromate and arsenite, the reaction starts. The initial products which are quickly formed by oxidation will be reduced by arsenous acid to bromide ion. Bromide enhances even more the rate of reaction, diffuses into the neighboring layers, and thus the reaction propagates. Addition of indigo carmine makes the propagation visible.

In all these cases, an event propagates in space, and it is not unlikely that the propagation of a nerve impulse is similar. Although this is just one potential explanation, it appears worthwhile to show that analogies exist for many incidents.

First, one should note that a nerve is temporarily exhausted after propagation of a stimulus. It takes a certain time to renew its potential, and this is evidence that a chemical reaction has occurred. Another indication that a chemical reaction has taken place can be found in the fact that, not only in the test tube but also in the nerve, the velocity of propagation decreases with a decrease in temperature.

An analogy for the so-called “threshold” for nerve stimuli can also be found in the test tube. Let us take the reaction HBrO₃ + AsO₃ as an example. To free the solution from the autocatalytically acting Br⁻, I have at times sterilized the solutions by saturation with AgBrO₃ so that the Br⁻ was bound and removed as AgBr. As a result, the solution contains small amounts of Ag⁺. If therefore, very little Br⁻ is used as a stimulus, it will react at once with the Ag⁺ to form AgBr and thereby is rendered inactive. It takes a certain minimal stimulus to initiate the propagation. On the other hand, several weak Br⁻ stimuli in rapid succession can use up the silver ions, decrease the sensitivity barrier, and then initiate propagation. A similar behavior is observed for a nerve stimulus.

Also, the nonspecificity of the stimulation of the nerve in contrast to the selective stimulation of the sensitive nerve endings can be found in our nerve model. Our permanganate—oxalic acid nerve can be stimulated by any reducing agent that reacts with MnO₄⁻. We may, however, transform this nerve into an “optic” nerve by placing one end of the permanganate tube in a flask filled with ferric oxide. Upon exposure to light ferrous oxide is produced, which, in turn, reacts with the permanganate and causes propagation of the stimulus.

Various other examples could be mentioned; one might even construct a chemical theory of memory, but in conclusion I will point to only one more analogy. The autocatalytic reactions have, as can be easily seen, a striking similarity with explosions. Here, as there, ignition proceeds from one spot. Here, as there, we have first a small and then an ever-increasing reaction rate, which, after it passes through a maximum, decreases again to an extent as the original reactants are consumed. In a way one can talk about isothermal explosions. The autocatalytic reaction between H₂O₂ and permanganate, which produces O₃, may even be used for the construction of an isothermal pistol. But that is child’s play.

More important from a practical standpoint appear to be the following facts. Nernst has recently pointed out with great emphasis that the control of explosive processes is important for the theory and practical development of gas engines. The same was said yesterday in Professor Will’s lecture on the propagation of reactions caused by explosives. The mathematical difficulties in dealing with nonisothermal explosions are substantial. It is my belief that the investigation of partial processes will serve as a first step to increase our knowledge of the time dependency of explosions in the gas and solid state. The investigation of adiabatic reactions has been started by Bredig. Together with Herr Meinecke, I have started to study the propagation of isothermal reactions in homogeneous medium.

I think therefore that our experiments in progress have a certain practical importance.

Discussion

Dr. Brode—Ludwigshafen a. Rh.: Rust catalyzes the oxidation of iron, a case which is very important in practical terms. Could this also be considered as one of your reactions, Mr. Speaker?

Professor Luther—Leipzig: I excluded heterogeneous reactions on purpose. Many such reactions are known, for example, the dissolution of copper in nitric acid that is free of nitrous acid, the activation of passive iron in an appropriate solution by touching it with an active iron wire, and other examples. But for my purposes, it is important to have totally homogeneous media.

Geheimrat Nernst (2)—Berlin: I want to allow myself one question. I want to point to the fact that physiologists have looked for possibilities to explain the rapid propagation of nerve stimuli and have pointed to the analogy with explosions. However, this is obviously a very different process because the propagation of explosions proceeds through a high temperature pathway, whereas the speaker has stressed the importance of isothermal propagation which is assumed to occur in the nerve. I am afraid that it is not possible to reach high velocities of propagation, like that needed by the physiologists, by this pathway. I would like to remind you that the propagation of a nerve stimulus is about 30 m/s (Interjection: 60). This results in 100 to 130 km/h, which is faster than the fastest train (“Blitzzugsgeschwindigkeit”).

We have, however, witnessed by looking at the beautiful experiments that you, Mr. Speaker, have demonstrated, that the propagation of a nerve stimulus is about 30 m/s (Interjection: 60). This results in 100 to 130 km/h, which is faster than the fastest train (“Blitzzugsgeschwindigkeit”).

Professor Luther—Leipzig: In principle, yes, but hardly experimentally because in general the “Wackeligkeit”, i.e., the self-decomposition of the solution, increases with the speed of propagation. For an autocatalytic reaction of second order the formula that I have written down here applies. The velocity \( v \) is equal to \( \alpha/\sqrt{D - C} \), where \( \alpha \) is a numerical constant between 2 and 10 and is dimensionless. The diffusion constant \( D \) cannot be increased substantially. Also, the concentration \( C \) cannot be increased substantially. However, the velocity constant \( K \) of the autocatalytic reaction can, in principle, assume any large value (3). Therefore, the possibility that we have extremely rapid autocatalytic reactions and that nerves use such reactions for their purposes cannot be discounted.

Geheimrat Nernst—Berlin: Who has derived this formula?

Professor Luther—Leipzig: Myself.

Geheimrat Nernst—Berlin: But this is not published yet?

Professor Luther—Leipzig: No, but it is a simple consequence of the corresponding differential equation.

Geheimrat Nernst—Berlin: Frankly, I cannot understand how one could obtain such high velocities, but one will look forward with even greater interest to the complete publication.
will have to limit ourselves to relatively slow reactions and small velocities of propagation.

**Geheimrat Nernst—Berlin**: As for the physiology, one has to point perhaps even more to the velocity of crystallization. Here we have nonisothermal processes that obviously can occur as fast as one wishes. However, this is true only for a heterogeneous system, as you have emphasized.

**Professor Bredig—Heidelberg**: I want to mention that there might be another possibility to explain nerve transmission. I think this explanation already exists, namely, to a large extent these are thought to be electrical phenomena on surfaces (according to Ostwald the surfaces are permeable only to certain ions). Most likely, changes in the voltage across the surface occur and, as a result, changes of the polarization state of such a surface will follow. For example, Bernstein in Halle a.S. has done extensive research in that direction, and also Borutta in Göttingen, and others. The equalization of differences in the electrical potential would be attained too quickly in the case they proceeded through the normal routes. But if we have only changes in the surface voltage, then these changes would propagate as waves across the surface maybe too slowly. In contrast, let us assume there is an electrical polarization on certain surfaces and at the same time a certain capacitance of the surface is added, then one could arrive at something of the right order of magnitude. The nerve currents have been explained in a similar way (Nernst, Zeynek, Barratt) as polarization phenomena.

**Geheimrat Nernst—Berlin**: But this is always based on a heterogeneous system.

**Professor Luther—Leipzig**: I want to add that Herman in Köningsberg has indeed constructed a purely electrical system made up of capacitors and self-inductances that propagates an electrical stimulus with a finite velocity that is by no means the velocity of light. And he closes with the following statement: Up to this point it is still not explainable how the stimulus is created in the beginning. I don’t want to insist that my explanation of the processes involved in nerve stimulation is the only possible one. I only say it is a potential hypothesis. If it is true, then it is fine, but if not there is nothing I can do and I must go on experimenting.

**Translator’s Comments**

1. The term “rep.” is an abbreviation of “respektive” meaning “or rather”, suggesting other possible reaction products. The mechanism of this reaction is now well established with the net process given by BrOCl - 35Br - 16H+ = 3HBr + Br2 + 3H2O.

2. Walther Nernst, discoverer of the third law of thermodynamics, was at this time professor of physical chemistry at Berlin. In 1881 he was appointed Geheimrat, that is, Privy Councillor. Nernst had been Ostwald’s assistant in 1887 to 1889. Luther became Ostwald’s assistant in 1896 and was, by 1900, director of the laboratory in Leipzig.

3. Second-order reaction rate constants do not exceed about 30³ M⁻¹ s⁻¹, the value for a diffusion-limited collision rate. For a typical diffusion constant of 10⁻⁹ cm² s⁻¹ and, for C = 1 M, Luther’s formula predicts maximal velocities of 10 m s⁻¹. No known chemical waves travel that fast; typical velocities are 10⁻⁴ m s⁻¹ (6 mm min⁻¹).

4. “Wackelig” is a colloquial term meaning “shaky, loose, wiggly.” Luther probably means that as one tries to increase the speed of traveling waves, the phenomenon disappears because the overall reaction in bulk occurs too soon.