

**Chemistry.** — “*Volta-Luminescence*”. By Dr. J. LIFSCHITZ. (Communicated by Prof. F. M. JAEGER).

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§ 1. On the passage of electric currents through Voltaic cells phenomena of light are often observed at the electrodes. This “electrolytic”, or rather this “electrode” light can appear both at the anode and at the cathode, as well on use of continuous current and of alternate current. The nature of the emitted light has seldom been investigated, and then only unsatisfactorily. Consequently so far only little could be said with certainty about the nature of the process. Some researchers (1, 2, 3) have interpreted some of these phenomena of light as reaction luminescence phenomena — hence as belonging to the phenomena of chemi-luminescence. If this should appear to be true, this would be of importance, because, as is known, ionic reaction is hardly ever attended with luminescence (4, 5). Besides the phenomena in question are of importance spectroscopically and electro-chemically. The light emissions under consideration may certainly not be considered as of an exclusively thermal character. For, as earlier experimenters already observed, the phenomenon of light is as a rule the more intense, as electrode and electrolyte have a lower temperature. Often the luminescence only occurs at very small intensity of the current. The spectrum is mostly discontinuous, or it presents at least a maximum of intensity, as is not possible with purely thermal radiation. At any rate an incandescence of the electrode metal can be distinguished with perfect certainty from the luminescence proper. Hence we are justified in distinguishing the phenomena in what follows as “Volta-luminescences”; and it will appear that inter se these are of very different characters, though on the other hand they resemble each other more or less in the following respects:

1. There is mostly a considerable increase of the resistance of the cells, as long as the electrode emits light.
2. Formation of solid or gaseous layers at the luminescent electrode, which sometimes entirely prevent the passage of the current.
3. Often an abnormal course of the electrolysis can be observed.

1. *Cathodic Luminescence.* (WEHNELT interruptor,  
Chroscope of v. BOLTON.)

§ 2. The first data about phenomena of light at the anode, as they appear in the WEHNELT-interruptor, were given by WEHNELT (6) himself. VOLLER and WALTHER found (7) that much stronger light effects are obtained when the smaller electrode is made cathode, hence when the interruptor is inserted reversely. A very pure spectrum of the electrode metal is then observed, and further some of the hydrogen lines appear. The phenomena also occur when the cell is not inserted as an interruptor, hence without induction coil.

Without taking these observations sufficiently into account, v. BOLTON (8) later described an arrangement which was suitable for spectralanalytic purposes and closely resembled the preceding one. He called this arrangement "Chroscope". As anode served a thick platinum wire or platinum plate; as cathode he used a platinum wire, or a rod of the metal that was to be examined spectroanalytically. The electrolyte ( $H_2SO_4$ , or better  $HNO_3$ , 1 : 4) contained in the first case a small quantity of the substance to be examined. When the current is closed by carefully immersing the cathode, very clear and pure spectra of the metals are obtained, which are present as electrode or in the electrolyte, and besides H-lines (especially  $H_\alpha$ ) and the Na-D-line. v. BOLTON used a potential of 110 Volt; then the strength of the current in his electrolyte-chroscope amounted to 0,15—0,3 Amp., in his metal chroscope to 2 Amp.

MORSE (9) investigated the light of the WEHNELT-interruptor more closely. He used an alternate current of a pretty considerable strength, and found that cathode and anode give the same spectrum; the cathodic light was, however, much stronger than the anodic light. He did not observe H-lines. The spectra obtained sometimes resembled the arc-spectrum more closely, sometimes the spark spectrum, without his being able to give a satisfactory explanation of this. There are, however, always characteristic differences between WEHNELT- and spark-spectra, resp. WEHNELT- and arc-spectra. We shall come back to further observations of MORSE later on.

For the investigation of the cathode spectra the arrangement of v. BOLTON is the most suitable; this was still somewhat modified for experiments of longer duration. Fig. 1 represents a simple model of an electrolyte-chroscope, with which experiments can be made without difficulties. A U-tube is placed within a cooling-jacket; the legs of this tube are closed by two rubber stoppers, in which

the electrodes are fastened. By means of an intermediate piece the two legs are connected with each other and with the water-jet suction-pump, which immediately removes the oxyhydrogen gas formed in the electrolysis. The luminescence is started by the immersion of the cathode, and at the same time the cell is closed air-tight. In the metal chromoscope the tube drawn in fig. 2 comes in the place of the *U*-tube.

In order to photograph the spectra, the light was thrown on the slit of a HILGER spectrograph by means of a small condenser with small focal distance. When Viridin-Inalo plates were used, the exposure had sometimes to be continued from 40 to 150 minutes, because spraying took place. As electrolyte  $\text{HNO}_3$  1 : 4 was generally used; other electrolytes, however, may equally well be used, e.g.

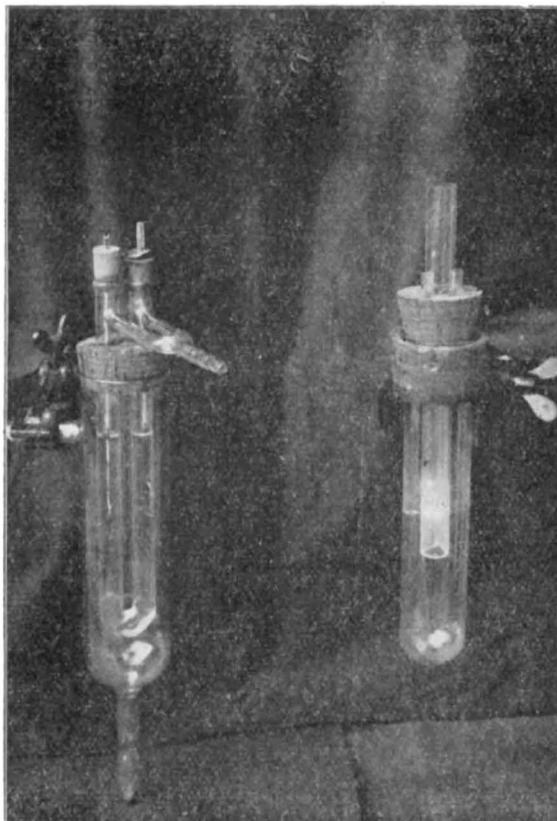
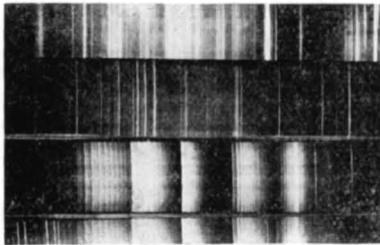


Fig. 1

Fig. 2

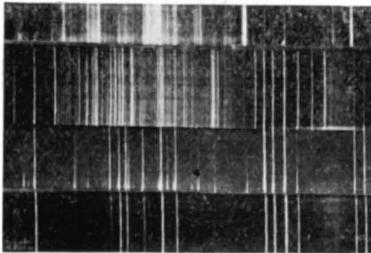
diluted or concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{KOH}$  etc.; this brings about no essential difference as to the nature of the phenomena.

**Al-spectra.**

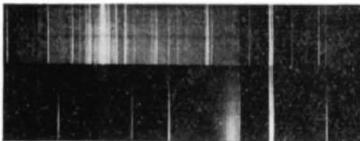


Spark.  
 Electrolytechromoscope.  
 Metalchromoscope.  
 Arc.

**Cu-spectra.**

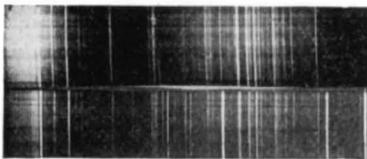


Spark.  
 Electrolytechromoscope.  
 Arc.  
 Metalchromoscope.



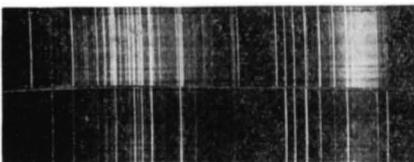
Mg-spectrum in d. electrolytechromoscope  
 Mg-arcspectrum.

**Strontium.**



Strong solution.  
 Dilute solution.

**Copper.**



160—180 V. 68 min.  
 < 100 V. 136 min.

Spectra obtained with the electrolytechromoscope.

Fig. 3.

§ 3. In contrast with what was found by MORSE, H-lines (especially  $H_{\alpha}$ ) were present in the emitted spectrum; further Pt-lines at platinum cathodes. *Apart from this it was stated that electrolyte and metal chromoscope, give totally different spectra, — a fact which was quite overlooked both by v. BOLTON and by MORSE.* When the metal that is to be detected, only occurs in the electrolyte, the spectrum very closely resembles that of the spark-spectrum of the metal. If this same metal is, however, immersed as cathode in pure acid, a spectrum is obtained which agrees closely with the arc-spectrum. As an illustration of these facts, which I could verify repeatedly, some photographs have been reproduced here (fig. 3).

That we are justified in speaking of a general behaviour here, follows for the rest, besides from our own observations (with Mg, Pb, Fe, Wo, Mo, Ta, Al, Cu etc.), also from the data of v. BOLTON and MORSE themselves. If the metal is at the same time in electrolyte and electrode, it is to be expected that a superposition of the two spectra is observed. Since, however, the metal chromoscopes produce more intense phenomena, it is easy to understand that MORSE observed a strong arc-spectrum that is generally superposed by a weak spark-spectrum.

If the chromoscopes are to function normally, a definite current intensity is required in both cases, which though dependent on the adjustments of the apparatus, always remained within the limits indicated by v. BOLTON. With Cu-salt in the electrolyte chromoscope (fig. 1) e. g. 0,4–0,5 Amp. appeared to be required. A greater intensity of the current caused incandescence of the wire, and the disappearance of the luminescence, whilst a weaker current caused the total light intensity to become smaller. As appears from the adjoined photographs, also a selective weakening takes place: some lines losing much more in intensity than the rest. The same effect may also be reached by greatly diminishing the concentration of the metal salt.

In many cases, especially when earth-alkali salts are used, one has the impression that the whole liquid at the cathode is luminescent. This effect is, however, not always found; besides the spectrum was not changed by this. The co-luminescence seems to be caused by still unknown accessory circumstances.

With regard to the mechanism of the emission process it may be considered as an established fact that the cathode is surrounded by a gas envelope. As already VOLLER and WALTER observed, this may be shown simply as follows: when a well-luminescent chromoscope is

first cut out, and then immediately inserted again, the luminescence quickly continues without it being necessary to take the electrode out of the liquid and immersing it again. If, however, we wait a short time after the cutting out, a hissing sound is heard after about 2 or 3 sec., and now the chromoscope is not at once luminescent again when it is inserted. Moreover the experiments of RIESENFELD and PFÜTZER (11) have described, plead still more in favour of the existence of a gas layer. There a small of light arc is formed between cathode and liquid, and I could verify that the same spectral phenomena are obtained as in the chromoscope. On use of Pt- or Ir-cathodes, the metal to be detected being present in the liquid, a spark-spectrum is obtained; when, however, the metal is used as cathode with pure acid, and arc-spectrum.

§ 4. Probably the following idea must be formed about the origin of these cathodic luminescence phenomena. Between electrode and electrolyte there is formed a gas envelope containing hydrogen, water-vapour and some oxygen; within this layer lies almost the whole fall of potential of the cell. The cations not being able to traverse this layer, there a current of rapid cathode rays is formed, which discharge these cations. The discharged metal atoms now get into the gas layer, and are excited to the emission of a spark-spectrum by collision with similar flying electrons.

The spraying of the cathode is greatly promoted by the impact with positive particles. If, as in the metal chromoscope, the current density and the strength of the current intensity are relatively high, also uncharged atoms of the electrode metal get into the gas layer — either because the spraying consists primarily in a scattering of molecular particles, or because locally a sufficiently high temperature arises —, and then an light-arc is formed and hence an arc-spectrum is observed.

If the electrolyte at the same time contains a sufficient number of ions of the electrode- or another metal, a spark spectrum of the second metal can of course appear by the side of the arc-spectrum of the first metal. This is, however, not necessary. Depending upon the nature of the electrode metal, the arc-spectrum is more or less apparent. Thus MORSE showed already that the spectrum of a platinum cathode is intense in solutions of acids and alkalies, but very faint in solutions of earth alkalies, while a strong aluminium (arc-)spectrum appears with an aluminium electrode in almost any electrolyte. The relations that are valid here must, however, still be examined; possibly the greater or less tendency to spraying of

the electrode material is playing here a prominent part. That melting-point and evaporation point of the metal are not decisive, has already been stated by MORSE.

(II) *Anodic Luminescence.*

§ 5. As might be expected, the phenomena at the anode are much more numerous and much more complicated than those at the cathode. Besides gas layers, also layers of solid substance can establish themselves here between electrolyte and electrode, thus causing luminescence. The sparks which appear in valve cells at the limiting tensions (10), have not been examined in what follows.

According to the nature of the emitted light and the cause of the luminescence at the anode, the following typical cases of luminescence can be distinguished.

1. Line- and band-spectra; to a certain extent these are very similar to those at the cathode, but they are generally much weaker.

2. Arc-spectra, equal to those at the cathode, but which can but rarely be obtained, and then only on definite conditions.

3. Generally a yellowish luminescence — which in so far as this can be ascertained, is spectroscopically continuous, — without formation of a layer of oxide or anything of this kind. The anode metal (or the carbon used as anode) gets shiny or bright.

4. For so far as this can be ascertained a continuous emission, with a maximum of intensity in a definite spectrum region; in this case the formation of solid layers at the anode always takes place.

First of all we will give some instances and some further particulars of the phenomena in each of these four classes.

§ 6. 1. Already VOLLER and WALTER record that at an interruptor anode from platinum in sulphuric acid 1 : 40, they obtained — by the side of the NaD-line — a faint band spectrum. If this cell contained sulphuric acid and also metal salts, the lines of these metals also appeared. The data of these investigators could be fully confirmed; no more than they, did I, however, succeed in determining more accurately the band-spectrum lying in the green<sup>1)</sup>. The intensity of the phenomenon was, indeed, too small for spectroscopic investigation, though it was always clearly perceptible, also in aqueous potassium hydroxide 1 : 10, and on use of other anode metals. Special phenomena were obtained on use of platinum anodes in sulphuric acid 1 : 40, containing at once several metallic salts.

In order to obtain anodic metal lines, greater quantities of metallic salt must in general be dissolved in the acid. Even then mostly a

<sup>1)</sup> Very probably these „bands” belong the oxygen spectrum.

few characteristic lines stand out very clearly (e. g. the green Tl-line; the three green Cu-lines). If the acid contains two kinds of metalions, often only one of these kinds of ions can be detected spectroscopically. An example of this is furnished by the following experiment:

A platinum anode was immersed in sulphuric acid 1 : 40, which contained a sufficient quantity of sulphate of sodium and sulphate of copper. First so much current was passed through that the anode wire became incandescent; then gradually resistance was inserted until the incandescence stopped and the characteristic yellow luminescence appeared. Only a very strong Na-D-line was observed then in the spectroscope. When gradually still more resistance was put in, the yellow luminescence and the Na-D-line became fainter and fainter, and the Cu-lines began to appear (in the green). At a definite terminal voltage green sparks were also immediately to be observed by the side of the yellow sparks at the anode.

It is exceedingly difficult to elucidate the nature of these very faintly luminous phenomena experimentally. It can only be stated that the luminescence appears to be caused by numerous sparks, and that there is undoubtedly a gas-envelope present also here, as already VOLLER and WALTER pointed out. Very probably a similar mechanism is to be supposed here as in LECOQ DE BOISBAUDRAN's "fulgurator". In this apparatus we have a layer of gas and vapour between anode and electrolyte, through which the sparks penetrate.

§ 7. 2. A beautiful and very intense anodic arc-spectrum can be obtained with an iron rod in hot concentrated or diluted sulphuric acid (sp. gr. 1.80 and  $H_2SO_4$  1 : 4); less easily by means of tungsten anodes in the same medium. Then the temperature of the anodes is pretty high; the colour of the emitted light is a brilliant blue. The tension in these experiments was 225 Volts. The emission did not appear until the luminescence described under 3 had been observed for a shorter or longer time. We shall, therefore, have to return to the said phenomenon presently.

3. A very peculiar light phenomenon is observed when the current is closed by immersion of a carbon- or metal-anode in concentrated or diluted sulphuric acid. The carbon then gets covered by a beautiful yellow mantle of light, which continues to persist for a long time; the carbon surface gets smooth, carbon powder and superficial impurities are removed. Metal anodes present an analogous behaviour, as was by observed by v. BOLTON (8), to whom we owe a method by this procedure for polishing and cleansing carbon electrodes. (14).

I have been able to corroborate the validity of this experimenter's results in every respect — both on use of concentrated and of diluted sulphuric acid. A digressing behaviour is shown only by typical valve metals (e.g. Al and Ta). These emit a white or bluish light.

For so far as could be ascertained, the spectrum of the yellow light is continuous; often the Na-D-line is still to be observed. After the experiment the electrodes surface is bright and smooth, but the electrode-diameter is mostly slightly diminished. The white light from valve metals is continuous, but on the boundary electrode-electrolyte-air sparks often appear then, which certainly emit line-spectra.

The terminal voltage during the yellow luminescence (in Cu, Fe, Mo, Wo, Ni, C) is about 100 Volts, the intensity of the current some tenths of an Amp., i.e. on use of wire-electrodes of a diameter of some mm., which were immersed 1—2 cm. deep. The temperature of concentrated sulphuric acid then rises very rapidly to the boiling-point, that of diluted sulphuric acid (smaller intensity of current) somewhat more slowly. When once the boiling-point temperature has been reached, the colour suddenly changes from goldish to brilliant blue; at the same time the current is reduced to less than 0,1 Amp., the terminal voltage rising to the total value available (225 Volts). Then the well known arc-spectrum of iron or tungsten is seen in the spectroscope. This experiment is very suitable for demonstration. Analogous phenomena can most probably also be obtained in other metals, though less easily.

§ 8. The appearance of an anodic arc of light particularly at hot anodes, is, indeed comprehensible; the yellow luminescence is, however, less easy to understand. A purely thermal emission of the metal cannot be supposed. Nor can there be any question of a reaction luminescence, since the light always possesses the same colour, no matter what anode material is used. VON BOLTON suggested that the anode gets covered with "a yellow incandescent" oxygen mantle. In fact oxygen can be brought to an emission of a yellow continuous light by an electric current at higher pressure (13). At lower pressure a maximum of intensity in the green or yellow green occurs in this continuous spectrum. It may, therefore, be assumed as very probable that our electrodes are surrounded by a mantle of oxygen generated electrolytically, in which the gas is brought electrically to light emission under pretty high pressure. At higher temperatures the pressure in this oxygen layer must diminish, perhaps the layer must become quite unstable, and finally conditions are reached which give rise to a metal arc of light.

§ 9. 4. Anodic light emission has often been observed during electrolyses, when an insoluble or sparingly soluble reaction product is formed at the anode. This product can then form either a solid layer firmly attached to the anode, or a layer that gets more or less easily detached.

The former can often be observed in valve cells. Already below the limiting tension a dullish white light may be seen at the valve anode (10), which becomes pretty intense under definite circumstances, (e. g. with Al-anodes in borax solution, Ta in diluted alkali or carbonate solution). With this emission of light should also be classed the emission of light of magnesium anodes in diluted alkali (15).

In all these cases the potential rises to the maximum value available, the passage of the current is almost entirely prevented. The luminescence begins very soon after the closure of the current, often with periodic oscillations of the intensity during the first minutes, and then continues to persist till the current is broken. The light emission is, however, generally soon prevented, when electrode or electrolyte are heated by the weak current that continues to pass. In prolonged experiments it is, therefore, necessary to ensure good cooling.

The light, which is almost always a dullish white, sometimes more greenish or bluish, appeared to be continuous on spectroscopic investigation.

It is also noteworthy that with magnesium anodes the maximum of light intensity is reached in potassium hydroxide 1 : 100; a very strong luminescence is also obtained by using an ammoniac solution of di-sodium phosphate instead of the hydroxide. In this medium also zinc anodes produce an exceedingly beautiful light emission, a borax solution being the most suitable electrolyte with aluminium. But also with aluminium and with tantalum diluted alkali hydroxide solution etc. can be used.

In these processes the electrolyte is covered by an adhering layer of the oxide or of another insoluble anode product, as this was already shown by other experimenters. The generality of such phenomena is brought out by the fact that always new observations of the kind described are being communicated (cf. e.g. 1a).

But also when no direct valve actions are to be observed, such phenomena of light are nearly always found when at the anode a sparingly soluble product is found. To these belong, among others, the following phenomena of luminescence which have partly already been known for some time:

Electrolyte	Phenomenon
KJ aq, saturated H <sub>2</sub> SO <sub>4</sub> conc.	a bright luminescence at anodes of Cd, Hg, Pb. " " " " " " " " Pb, Al, Ta; Mg gives a short flash; at Cd anodes there is seen a ring of light, which moves up and down.
KOH aq, strong	Fe (a bright luminescence, but which cannot very easily be examined on account of strong foaming), Ni (very slight intensity of the current).
Na <sub>2</sub> HPO <sub>4</sub> NH <sub>3</sub> aq	Cu gives a circle of sparks.

Exceedingly intense is the luminescence at an Hg-anode in saturated KI-solution at sufficient density of the current. The bright anode-surface is covered with a thin layer of mercury iodide immediately after the closure of the current, and then begins to emit a golden light. After a short time the intensity of this light reaches a maximum, and then diminishes again. By renewal of the mercury surface, either by stirring or by allowing the mercury to overflow from a funnel-shaped anode vessel, etc. the luminescence can be restored with full intensity.

In agreement with former experimenters (2) the spectrum of the emitted light was found to be continuous, with a maximum of the intensity in a definite spectral region. WILKINSON (2) has pointed out that the colour of this light also agrees with that of the light emitted by the anode product in question, when it is bombarded by cathode rays.

§ 10. It is exactly these kinds of luminescence that are very often considered as reaction luminescence (chemi-luminescence). Formation or decomposition of the anode products were thought to be accompanied by a luminescence which could reach a considerable intensity with sufficient reaction velocity<sup>1)</sup>. BANCROFT (1) and his pupils, also WILKINSON (2) have endeavoured to give support to this view. In the course of our own observations on comparison with those of other investigators it appears, however, that this conception is untenable.

In the first place it can be established that all the phenomena described in this chapter, are related. And this not only because they appear to be of the same nature spectroscopically, but also because their occurrence always appears to be bound to the formation of sparingly soluble or insoluble anode products.

<sup>1)</sup> On this conception compare (5).

Premising this, it may be inferred from a pretty great number of reasons that a conception of these luminescence phenomena as reaction luminescence phenomena must be considered as erroneous.

In the first place with this view of the matter it cannot be explained why only formation of insoluble products gives rise to luminescence. It can, indeed, be predicted that the probability of anodic luminescence and its intensity will be the greater as the anode-product dissolves with the greater difficulty. For it appears in particular that on formation of readily soluble anode-products, luminescence never seems to be observed.

Nor can the considerable increase of intensity of the luminescence at low temperature (hence at smaller reaction velocity) be accounted for on the ground of the said conception. For with valve anodes the luminescence is by no means most pronounced on particularly strong anode-reaction, but only when the excluding layer is as stable and homogeneous as possible, and is attacked as little as possible by the electrolyte. Thus magnesium emits the brightest light in *diluted* KOH, aluminium in borax solution, which would certainly be unaccountable in the case of real "chemi-luminescence". A magnesium anode is particularly strongly attacked by diluted sulphuric acid, though all the same, there is no luminescence at all to be observed.

Moreover it remains inexplicable how anodes which are rapidly covered by an insoluble layer, yet continue to emit light. It might much sooner be expected in this case that the light would cease after the formation of a covering layer. But this is by no means observed in the majority of the cases.

Finally the increase of light intensity after the closure of the current, as is particularly clearly observed with mercury anodes in KI-solution, is unaccountable in a reaction luminescence. For, how a certain quantity of reaction products would be able to increase a direct chemi-luminescence, is not clear. Nor can periodic and rhythmic light emissions (Cd in KI-solution, Mg immediately after the closure of the current) be accounted for in this way.

§ 11. The only conception which can be brought to harmonize with all the experimental facts, is in contrast with the conception discussed just now, in my opinion the following: at once after the closure of the current a layer of reaction products is formed at the anode, which hampers the passage of the ions to the anode, or renders it impossible. Then the electric discharge of these ions takes place (at sufficiently high potential) under the influence of split off

anionic electrons, which fly through the anode layer with strong acceleration. By this the matter in this layer is brought to luminescence in the same way, hence with emission of the same spectrum, as this would happen by means of cathode rays. If the layer becomes too thick, higher potentials will be required to bring about a passage of the current, and finally current could only pass in certain cases when the layer is traversed by sparks (limiting tension with anodes). When on the other hand the layer is attacked by the electrolyte in some way or other, it is very well possible that also the light emission at the anode can vary locally, and in particular the periodic oscillations of the intensity along the anode become possible. Increase of temperature will always hamper the luminescence, either because the solubility of the anode product is in general increased by it, or because the layer is rendered less stable by it in mechanic respect. If the anode layer has little mechanical stability in itself (e.g. mercury iodide), a certain minimum current density will be required to form a coherent layer with sufficient velocity, and to allow this to continue to exist, in spite of continued decomposition.

By this conception also the analogy between the anodic and cathodic luminescences is clearly brought out.

Summarizing we may say that also in these anodic luminescence phenomena, as this was earlier shown for ordinary chemi-luminescence (5), not the anode-reaction in itself takes place with light emission.

It must rather be admitted that first reaction products are formed which are brought to emission, in this case by means of the electric energy of a source of current outside the system examined<sup>1)</sup>. Hence there is no question of an ion reaction, which takes place with light emission, and of a departure from the general rule that it is just these reactions, which proceed practically with infinite velocity, that are never accompanied by a light-emission.

The above considerations show further that VOLTA-luminescence occurs very frequently, but also that it can be of a very different character. On further investigation of these phenomena it will be necessary to distinguish these kinds of VOLTA-luminescence scrupulously. The present investigation may be considered as a first attempt at reconnoitring the ground in this respect.

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<sup>1)</sup> In cases of common chemi-luminescence the reaction itself furnishes the energy necessary to excite to light emission some of the kinds of molecules present in the system. (see 5).

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