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**Physics.** — "*On the light emission of gases and mixtures of gases by electric discharges.*" By Dr. L. HAMBURGER. (Communicated by Prof. H. KAMERLINGH ONNES.)

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§ 1. *Method of investigation.*

Researches on the influence of different factors in the emission of light of gases by electric discharges have revealed phenomena of so very different nature, that we strongly felt the desirability of systematic methods of investigation and of objective measuring methods that are free from the imperfections of the human eye.

As however in spectroscopy and the measuring of intensities which is closely connected with it, great difficulties arise, we should have to wait a very long time for results if we wished to measure the intensities of each emitted wavelength (spectral line or band) for the different gases and mixtures and then still under different circumstances. Therefore on entering this difficult and vast domain of research our first work can only be a first exploration of the new field of investigation, which work renders a method desirable which allows a quick survey of what is observed under different conditions. Such a method is the photographic one, which can also be used in the ultraviolet part of the spectrum and which has been described in a recent publication of G. HOLST and L. HAMBURGER.<sup>1)</sup>

In the two next paragraphs of this short paper a survey is given of the most important results of an investigation made in this way on the influence of different factors on the emission of light of gases and mixtures by electric discharges. The lighting of the gases was excited by a continuous current discharge apparatus the construction of which is based upon the direction lines determined by H. KONEN and W. JUNGJOHANN<sup>2)</sup> and in which (comp. J. SCHWEDES<sup>3)</sup>) streaming gases are used. By the application of streaming gases several phenomena could be investigated which up till now had not or hardly been observed.

The sector method alone, described in the publication of G. HOLST

<sup>1)</sup> These Proceedings, p. 1021.

<sup>2)</sup> Verh. d. D. phys. Ges. (12) **3**, 128—144 (1910).

<sup>3)</sup> Zeitschr. f. wiss. Phot. **11**, 199 (1913).

and L. HAMBURGER, does not allow to compare the intensities of the radiations of different wavelengths. This can be done however by determining the selective action of the optical arrangement and of the photographic plate.

For this purpose it proved in some definite cases desirable to illuminate the sensitive plate, whilst using the rotating sector, with known temperature radiators, which work at a very high temperature and the energy-curve of which is known. The sensibility curve arising after the development (fig. 1, plate I) was then compared with the energy-curve following from the well-known laws of radiation. In this way the change of sensibility of the plate with the wavelength could be determined.

Those who want to know more about the subject, must be referred to my dissertation <sup>1)</sup>, where moreover a collection of objectively reproduced emission spectra of a considerable number of gases and their mixtures will be found, which at first sight give an impression of the distribution of intensities, such at least as has been represented on the photographic plate. Such a collection was wanting until now in the literature on the light emission by gases.

## § 2. *Measurements of intensity for pure gases* <sup>2)</sup>.

Investigations were made on the following gases: nitrogen, hydrogen, argon, neon, helium. As an example we shall first give a more detailed discussion of the result found with nitrogen. We shall however begin with referring to the spectrograms represented in fig. 2. plate I. The first one is obtained by the action of light emitted by nitrogen, when in front of the slit of the spectrograph a wedge of smoked glass has been placed. The other one has been made with the rotating sector. This reproduction is a good illustration of the very strong selective power of the wedge of smoked glass.

### A. *Nitrogen.*

It may be allowed to mention in this place only the conclusions we got from the observations on the sharp edges of the bands of the second positive nitrogen group:

1. The measurements can be reproduced. 2. The influence of the time of illumination on the length of the edges of the bands is in agreement with the calculations. 3. The emissive power of nitrogen

<sup>1)</sup> L. HAMBURGER. Diss. Delft. 1917. In one chapter of this dissertation my experiments in the phenomena shown by *Tesla*-discharges in gases have been described.

<sup>2)</sup> For comparison with the measurements known in the literature see my diss.

is proportional to the supplied energy. 4. As to the pressure of the gas the following conclusions are drawn from the measurements.

a. For constant current density the intensity of the light decreases with a decrease of the pressure for the investigated range of pressure.

b. At the same time the maximum of the emitted energy is shifted towards the shorter wave-lengths.

c. At a change of the pressure of the gas the bands belonging to the negative pole show a characteristic difference in behaviour with the bands of the second positive nitrogen group which surround them.

d. The potential gradient in the positive column decreases with decrease of pressure and also with increase of intensity of the current.

e. At the side of the cathode the passage of a current gives rise to a decrease in pressure, which for high values of the current density is relatively great; the value of this pressure effect proves to be (approximately) proportional to the intensity of the current. This effect is opposite to the very small pressure increase found by A. WEHNELT and J. FRANK<sup>1)</sup> under special conditions; it has been observed for the first time here in a spectral tube and it offers — especially when the dimensions of the apparatus would be chosen with a view to this purpose — a means to learn something about the properties (mass) of the gas particles that conduct the current. It has been proved, that we have to do here with a physical effect and we may directly draw the conclusion that the negative ions are no electrons but electric particles with a relatively large mass. From a more detailed investigation we learn that to this phenomenon there corresponds an increase in pressure at the anode. The pressure effect is smaller in gases with lower molecular weight. It is apparently possible to bring these different things into connexion with the difference in mass, number, velocity of the negative and positive electrons (mass-transport by the electric current).

#### B. *Hydrogen, neon, helium.*

The observations made on these gases are in so far in agreement with those on nitrogen, that here we may draw the general conclusion, that within the limits of possible observation errors (and within the domain of investigation) the intensity of the spectral lines or bands of all gases investigated is proportional to the supplied energy and that with decrease of pressure the maximum of energy is shifted towards the ultra-violet. Moreover we learn from the observation

<sup>1)</sup> Verh. d. D. phys. Ges. 12, 444, 1910. See also J. STARK, BOLZMANN Festschr. 399, 1904.

that in the method used we have a very good means to discern between lines or bands belonging to different "carriers".

### C. Argon.

The spectral properties of this gas are widely different from those of the preceding elements. It is a well known fact that Argon gives a red and a blue spectrum. The representatives of the red and the blue spectrum show a totally different behaviour with respect to the supplied energy as is evident from the graphical representation in fig. 3<sup>1)</sup> of the connexion between the intensities of the light and of the current for the red and the blue spectrum of argon.

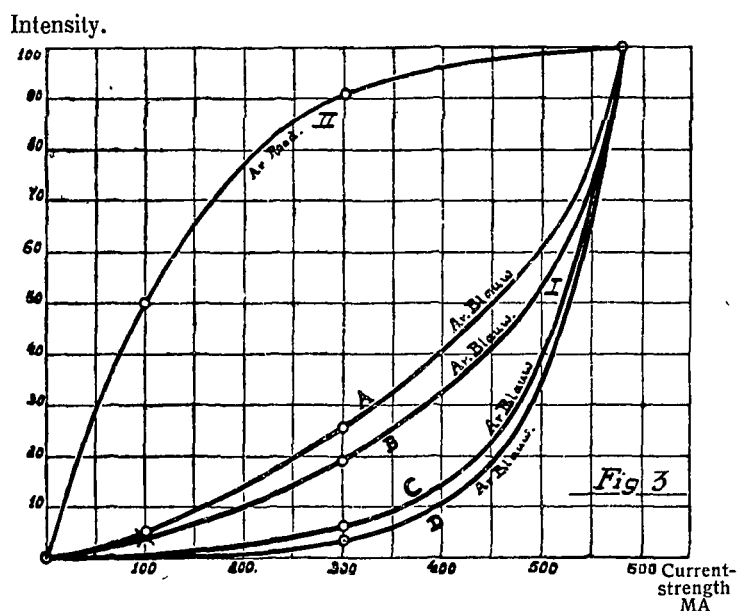


Fig. 3.

Also by changing other variables we find back this difference in behaviour.

### § 3. Measurements with binary mixtures.

The observations on gaseous mixtures show a pronounced difference between those mixtures, between the components of which reactions *can* take place and those for which this is *not* the case.

<sup>1)</sup> This figure is a good confirmation of the visual observations of P. G. NUTTING and O. TUGMAN (Bull. Bur. of Stand 7, 62 (1911)).

A. *Mixtures of gases which do not give reactions.*

Investigations were made with the binary systems argon-nitrogen, neon-nitrogen, argon-hydrogen, neon-helium, and argon-mercury.

While visual measurement by former investigators had founded the opinion that for gaseous mixtures the spectral behaviour is by no means an additive property with respect to the components, our research has rendered a slight change of these conceptions desirable. Let us first stipulate however, that the conceptions following from the above mentioned non-objective investigations doubtlessly contain a fundamental truth, especially there where the ionisation tensions of the components are widely different<sup>1)</sup> resp. where we have to do with highly electro-negative gases. In the last case however there occurs complication by chemical reactions.

Our investigations have taught us however to be careful not to exaggerate the conception, that the spectral behaviour of gaseous mixtures is by no means additive with respect to the components. At a definite total pressure the mixing of gases gives rise to a lower (partial) pressure of the components. And it proves to be a general phenomenon, that a decrease in pressure causes a shift of the light-emission towards the ultra-violet. With other words when gases are mixed visual observations will give the *impression* that the spectrum of one of the two gases strongly vanishes especially when the emissive intensities of the components are very different.

B. *Mixtures of gases which react with each other.*

The systems nitrogen-oxygen, nitrogen-hydrogen and nitrogen-carbon-monoxide were investigated. In each of these three cases the reaction took place by means of an electric discharge. Each time this chemical reaction was found to be accompanied by the occurrence of new bands in the spectrum. As for the system  $N_2-H_2$  this had never been sharply proved in a spectral tube<sup>2)</sup>. We subjected it to a detailed investigation, which supported the conception that the "electric ammonia-synthesis" is preceded by a disintegration of the reacting molecules into atoms. Further it proved possible to indicate conditions under which the ammonia-yield was many times higher

<sup>1)</sup> Comp. J. FRANCK and G. HERTZ, Verh. d. D. phys. Ges. 18, 213 (1916)

<sup>2)</sup> Already in 1891 J. M. EDER mentioned the occurrence of new bands in the neighbourhood of  $\lambda = 3359 \text{ \AA.}$  in the spectrum of the ammonia-oxygen-flame. (Anzeiger d. k. Ak. d. Wiss. Wien, 1891. See also Denkschr. d. kais. Ak. d. Wiss. Wien 60, 5, 1893.

than had ever been found. Photographs of discharges through flowing ammonia-gas confirmed the spectral part of the investigation of this system. For a more detailed discussion of the obtained results in connexion with the well-known theoretical considerations of J. FRANCK and G. HERTZ and J. STARK we must refer to our dissertation. Some points, both photographic and spectral, will be further discussed in a later paper of the author.

The author gladly accepts this occasion to express his gratitude to Dr. G. L. F. PHILIPS who kindly enabled him to make this investigation and also his great indebtedness to Prof. W. REINDERS and Prof. L. H. SIERTSEMA for their helpful interest in the work and the preparation of the writer's dissertation, from which this short paper is extracted.

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Fig. 1.

Spectrum of glowing Tungsten obtained with the aid of the rotating sector-disc etc. on Wratten & Wainright's panchromatic-plate (Copper-comparison spectrum).

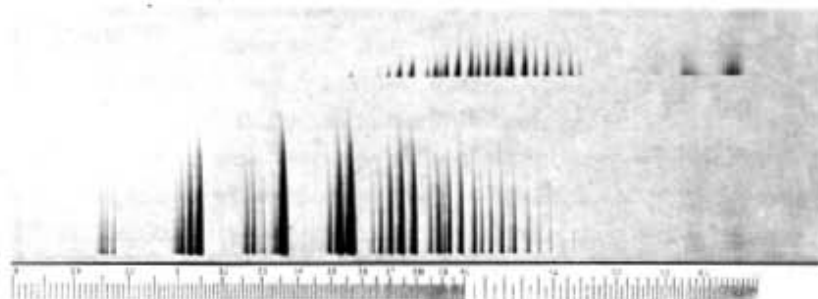


Fig. 2.

Comparison of the nitrogen-spectrograms, obtained with the aid of the rotating sector-disc, resp. the wedge-method.\*)

\* In the visible part of the wedge spectrogram (spectrum 2, fig. 2) some bands there occur that are wanting in the sector-spectrogram. The time of exposition however was in the latter case much shorter.