LETTERS TO THE EDITOR.

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The Brilliancy and Intensity of the Cupric Chloride Flame Spectrum.

IN the account of an interesting investigation of the flame spectrum of cupric chloride communicated by Peter Kien (*Zeits. f. wissenschaft. Photographie*, 1908, vol. vi., 337) there occurs a sentence to the following effect:—

"How difficult it is to decide upon the brilliancy and intensity of a spectrum by means of photography may be shown by the following example:—

"Prof. Hartley has published a very beautiful small photograph of the cupric chloride spectrum, the only one, moreover, which up to the present has been published. It is not in the least over-exposed, notwithstanding that Hartley gave it an exposure of two hours. My photographs were over-exposed in ten minutes—even if, as Hartley did, I brought cupric oxide into the oxygen and coal-gas flame saturated with chloroform vapour."

I think it is due to the author and others to point out that he writes under a misapprehension, inasmuch as his spectra and mine were taken each in a different manner and with a different object in view. He desired to photograph the best spectrum obtainable from the chloride for the purpose of measuring the bands, and therefore burnt the usual rolls ("cigarettes") of filter paper containing either cupric chloride or the oxide. The "cigarettes" were pushed by a spring through a tube into the flame at a speed regulated by a clock-work arrangement.

When communicating a paper on some devices facilitating the study of spectra (*Sci. Proc. Roy. Dublin Soc.*, vol. xi., p. 237, 1907), I demonstrated the extreme delicacy of the cupric chloride reaction in explanation of the reason that, although there may be no green coloration of the flame by copper, nevertheless the blue flame and cupric chloride bands are seen when salt is thrown into a fire of glowing coals.

The experiment was made in the following manner:—a quartz fibre about a millimetre thick was placed in a solution of a copper salt and heated in the flame of the Meker (or Mecke) burner supplied with coal-gas, which was burnt with a blast of air at a pressure of about 700 mm. of mercury. The fibre was heated until all the copper salt had been decomposed, as shown by scarcely any evidence of a trace of copper being visible in the flame when looked at in a darkened room. On diverting about one-third of the coal-gas through the flask containing sponge soaked in chloroform, the hydrochloric acid produced by the combustion of its vapour yielded a large and brilliant blue flame due to the cupric chloride, which was steady and continuous for a long period. For the illustration of the text of the paper the first exposure of the copper oxide was limited to two hours, then, without removing the fibre from the flame, the chloroform tap was turned on, and a similar exposure made.

An excess of hydrochloric acid prevents the spectrum being visible at all, so that with the large volume of nitrogen in the air, and the consequent reduction of temperature arising from the hydrochloric acid in the coal-gas flame, the proportion of chloroform vapour must be limited, and the resulting quantity of cupric chloride vapourised is correspondingly small.

In the experiments made by Kien, the greater intensity of photographic action is caused by the use of oxygen under pressure along with coal-gas, whereby, in consequence of the much higher temperature and greater quantity of heat, he is able to feed the flame with a much larger proportion of chloroform vapour, and consequently to volatilise a very much larger quantity of cupric chloride in the same period of time than is possible with the air blast. Furthermore, by the use of the "cigarette," he has a larger quantity of copper in the flame at any given moment.

As a rule, my flame spectra are obtained by using the

oxy-hydrogen blow-pipe, and when the hydrogen is mixed with chloroform the photographic period of exposure, according to circumstances, varies from thirty seconds to five minutes.

That salt is decomposed and hydrochloric acid formed by the action of water vapour when salt is thrown into a coal fire is certain. It is proved by the fact, which I found out when studying this spectrum in 1887, that the characteristic blue flame is not obtainable when salt is thrown into a fire of charcoal. In 1890 Salet proved the origin of the blue flame to be cupric chloride (*Comptes rendus*, ex., p. 282), and not in any way connected, as had been suggested, with the spectrum of carbon, carbon monoxide, or hydrocarbon flames, nor due to the element chlorine or to hydrochloric acid. My interest in the matter thus came temporarily to an abrupt termination, because, having by this time become aware that minute quantities of copper are to be found in most metalliferous and many other minerals, also in acids, it was easy to account for the blue flame being frequently seen by reason of the extraordinary delicacy of the cupric chloride flame reaction. Coal ashes always contain copper, the origin of which is commonly pyrites, and in the fire this is speedily burnt to oxide. Sulphur dioxide, steam, and air, even below a very dull red heat, convert salt into sodium sulphate and hydrochloric acid, and hence the formation of cupric chloride in presence of an excess of hydrochloric acid. Kien's paper gives an admirable historical account of the subject, which is particularly interesting owing to the extraordinarily illusive and elusive character of this spectrum. Much of this may be read in the *Phil. Mag.* (4), vol. xxiv., 417-9, and the pages of NATURE during 1876 and 1879.

A very beautiful engraving of the cupric chloride bands is given in Lecoq de Boisbaudran's "Spectres lumineux," published in 1874.

W. N. HARTLEY.

Royal College of Science, Dublin, February 11.

On the Radio-active Deposits from Actinium.

IN the course of some experiments which Mr. W. T. Kennedy has been making at Toronto during the past few months, he has found a marked similarity in the active deposits obtained on positively and negatively charged electrodes placed within an air-tight vessel and subjected to the influence of the active emanation issuing from a sample of actinium.

In his experiments the electrodes consisted of two small circular brass discs provided with guard rings of the same metal, and placed parallel to each other at a distance of 2 mm. apart. The discs during an exposure were placed with their planes vertical and directly over an open metal tube 1.5 mm. in diameter, with the edges of the guard rings almost in contact with the edges of the upper end of the tube. The salt used was carried in a small tray which could slide freely up and down the tube, and by means of a clamp be supported at any required distance from the discs.

In carrying out a set of experiments on the effect of varying the pressure of the air in the vessel containing the discs and the salt, it was found at high pressures that the active deposit appeared almost entirely on the negative electrode. As the pressure was decreased, however, the active deposits on both electrodes increased, and ultimately at certain definite pressures, which were different for the two electrodes, reached maximum values. When the pressures were still further lowered, the amounts of the deposit received on both electrodes rapidly decreased, and finally approached equality. Up to the present the lowest pressure used is $\frac{1}{2}$ mm. of mercury, and at this pressure the deposit on the negative electrode was found to be only about 3 per cent. greater than that obtained on the positive. From the rapid character of the decrease in the amounts of the deposit obtained at the lower pressures, it seems highly probable that, with the arrangement of apparatus used, and the relative distances between the parts adopted, both electrodes would fail to show any activity, or at greatest a very small one, if the air were entirely removed from the exposing vessel.

In a particular experiment with the salt at a distance of 1 cm. from the disc electrodes, a maximum activity was