Experiments on Luminous Vapours from Mercury Arc

BY

MELA RAM, M.Sc.
Assistant Professor of Physics, F. C. College, Lahore.

AND

KARAM CHAND NANDA, M.Sc.
Lecturer in Physics, D. M. College, Moga.

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ABSTRACT.

Experiments on the luminosity of the mercury vapour distilled from mercury arc point to the fact that positively charged mercury atoms are responsible for the phenomena. The life of afterglow has been determined and found to be 0·03 sec., indicating the probability of the entities in the afterglow being metastable mercury atoms. The question of the most probable value of the energy content of the atoms in the afterglow is discussed from spectroscopic data and the value thus obtained is 14·8 volts. Observations made on the decay of the intensity of the afterglow are found to be consistent with the hypothesis put forward here.

I

Introduction.

The luminosity of the vapours distilled from a mercury arc was first observed by Stark [1] and subsequently investigated by various other workers. [2] Strutt who followed up

[1] J. Stark, Ann. der Physik, Vol. 14, p. 530, 1904.
[2] Matthias, verh. d. Deu. Phys. Ges., Vol. 12, p. 754, 1910.
Child, Phil. Mag., Vol. 26, p. 906, 1913.

this work was able to show later that the same phenomenon could be observed in the vapours of a large number of other substances. However, in spite of the fact that a good deal of experimental data is available, much still remains to be done, to elucidate the exact nature of the entities responsible for this effect, and it was with a view to throw some more light on the subject that the experiments described in the present paper were undertaken.

II

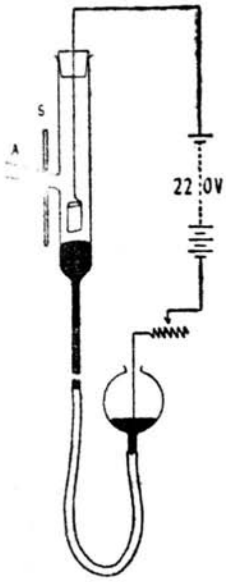

Fig. 1.

The general form of the apparatus employed is in principle similar to that used by previous workers and is shown in fig. 1. An arc is struck between a tabular iron electrode and the top of a barometric column of mercury contained in pyrex glass tube, by raising the level of mercury, lowering it again and keeping at a distance of about 2 cms. from the electrode. The current is kept at a value of about 5 amps. Though a smaller voltage can be used, it was convenient to work with 220 volts, with suitable resistances in the circuit. The terminal voltage perhaps does not exceed 80 volts. The vapour enters the side tube A connected to an exhaust pump, which keeps continuously running at low speed, and keeps glowing to a considerable length provided the glow tube is heated to a sufficiently high temperature. It is desirable to keep the side tube slightly inclined so that the mercury after being condensed may flow back to the reservoir. Since, however, it is very difficult to stop a certain amount of vapour going to the other side, a mercury catch is always provided between the pump and the tube. An asbestos screen S prevents the strong light of the arc interfering with the luminosity of the mercury vapour.

With this arrangement a number of experiments recorded by the previous workers were repeated and the results confirmed. It was found that on putting the electrodes across the side tube immersed in the vapour, a saturation current of about ·5 milliamps. passed through the circuit even when the voltage applied is 20 or 30 volts, showing the existence of ions. That the luminosity is intimately connected with these charged particles can now hardly be doubted. For when a wire-gauze electrode was placed in the tube A, it was observed that when no voltage was applied on the electrode, and it was kept insulated the luminous vapour passed through it. However, as soon as this was earthed, no luminosity could be detected beyond this point. On inserting two wire-gauze electrodes in the side tube, placed one after another at a distance of about 5 cms. the glow of the stream of mercury vapour stops only at the negative terminal. If the electrode nearer the arc is made positive, and the other negative, the luminosity passes through the gauze undiminished but comes to an abrupt ending at the negative electrode. When the polarities of the electrodes are interchanged the region between them remains dark. If now the potential difference is slowly increased, although the glow does not enter the electric field, a faint luminosity is set up at about 60 volts. This starts from the anode and proceeds towards the cathode. It is much bluer in colour than the after-glow, and becomes more prominent and much longer when either the side tube is heated or the rubber tube leading to the pump is pinched. These facts, which have been obtained in a very similar form before,[3] will help us in

[3] R. J. Strutt, Proc. Royal Soc. A., Vol. 91, p. 92, 1915

understanding the real significance of the after-glow, and are consistent with the view that the particles are positively charged. We shall discuss them more fully later. Measurement of current which flowed between the electrodes when the glowing vapour passed into the space between them was only a small fraction (about ·1) of that which passed when no glow was visible on reversing the polarity. And the result is not affected when the potential difference is small, or is so high as to start the subsidiary glow from the anode to the cathode. This result may appear surprising, but it adds additional weight to the view that the carriers are positively charged, though the current is mainly due to the negatively charged particles. So that even when the positive ions are removed the current does not change, though the luminosity is completely quenched. On removing the negatively charged particles, the current falls to a low value but the glow remains undisturbed.

We may in passing record an observation that the glow is quenched the moment the side tube through which the vapour is passing is heated, although a certain amount of heating of the side tube is necessary in order to make the glow travel over a long distance, for otherwise the mercury vapour is prematurely condensed. The quenching is observed only so long as the flame is applied to evaporate any globule of mercury condensed, and the glow reappears when the whole mercury has evaporated away. The moment the burner is removed the glow starts much more vigorously. It was at first thought that the cause of this may be somewhat similar to that which obtains in the case of active nitrogen, where it is well known that a preliminary 'cleaning up' of the glass tubes by the 'activated nitrogen' itself is necessary for a proper luminosity of the after-glow. In mercury probably it is due to the greater local pressure when the flame is applied, so that the glowing vapour is pushed back into the arc.

III

Effect of afterglow on other substances.

Lord Rayleigh[4] has studied the effect of the after-glow of mercury vapour on the vapours of sodium, magnesium, calcium, zinc and cadmium on the basis of Klein and Rosseland's[5] theory of collision of the second kind, with a special apparatus in which in addition to mercury other metals could also be used. For mercury he found that Ca, Zn, and Cd could be made to emit lines corresponding to about 9 volts. In Na and Mg no lines beyond those corresponding to 4·57 and 5·07 volts respectively, could be observed. In the case of Na this can be explained, for the ionisation potential of Na according to the measurements of Foote, Meggers and Mohler[6] with electronic tubes, and the spectrum analysis of K. Majumdar[7] is 45 volts, and the resonance lines do not appear in the near ultra-violet but at 376·6 and 372·3A units, which corresponds to a radiation potential of 32·8 volts. It is evidently justifiable to assume that whatever else the value of the energy of the excited mercury atoms responsible for the glow may be, it does not exceed, and is possibly much less than 32 volts. This sets the higher limit to the energy content; the lower limit evidently being 9·2 volts.

We have attempted to determine the effect of the afterglow on the vapours of organic liquids, to see if

[4] Rayleigh, Proc. Roy. Soc., Vol. 112, p. 24, 1926.
[5] Klein and Rosseland, Zeit. f. Physik, Vol. 4, p. 46, 1921.
[6] Foote, Meggers and Mohler, Astrophys. J., Vol. 55, p. 145, 1922.
[7] K. Majumdar, Ind. Jour. of Phys., Vol. 2 pt. 3, p. 343, 1928.

these are also excited. The apparatus used is diagrammatically shown in Fig. 2. and is self-explanatory. Carbon disulphide, alcohol, sulphuric ether, aniline, toluol and benzene were used, and it appears surprising that no luminescence whatsoever was observed as examined with a direct vision spectroscope. It may be, the effect is present in the ultra-violet or infra-red, but the regions were not investigated.

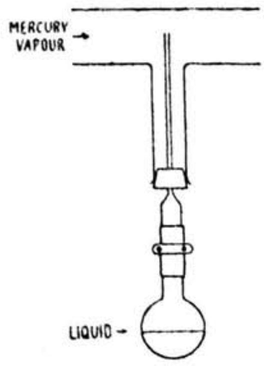

FIG. 2

IV

Life of after-glow.

In view of the interest that has recently been shown on the life of the excited atoms particularly in the metastable states, it seemed worthwhile to measure the life of the after-glow, and for this purpose therefore the following procedure and apparatus were adopted. The details of different parts of the apparatus will be clear by a reference to fig. 3.

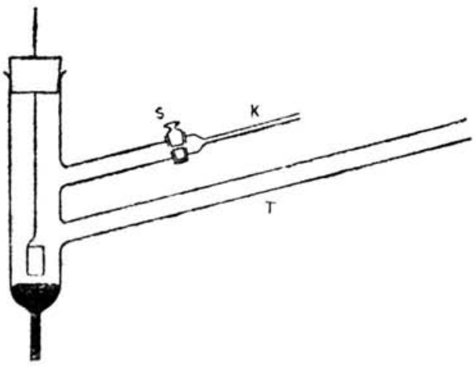

FIG. 3.

The tube T through which the mercury vapour passed was made about 75 cms. long, in order to accommodate the largest possible column of the vapour. Just a little above this and near the top of the tube in which the arc was struck, was sealed on another tube with two limbs one of which was connected to high pressure Mcleod gauge and the other was employed as an inlet for air or nitrogen through a stopcock and capillary tube K. The vacuum pump employed was a Gaede rotary oil pump provided with a nozzle for collecting the exhaust gases. The arc was first struck at 5 amps. keeping S. closed. The side tube T was heated and the maximum length to which the glow could extend was noted. The reading of the Mcleod gauge at this stage indicated the maximum value of the vacuum to which the pump could go. The stopcock S was now slowly opened, and the air allowed to stream in. As the pressure of the air increased a certain stage was reached at which the pressure of the air exceeded the pressure of mercury vapour, and the afterglow just stopped. The Mcleod gauge was now again read. The difference between this and the former reading was taken to be the pressure of the afterglow. The volume of the air admitted in the apparatus in a given time was then determined by collecting the exhaust gases over water, from which the volume of the air passing through the side tube in one second at the reduced pressure existing there, can be calculated, assuming the validity of Boyle's law under these conditions. If now the diameter of the tube and the length of the afterglow are known the life of the afterglow can at once be calculated. In one experiment the following set of observations were recorded.

Length of the glow	=20 cms. of Hg.
Pressure recorded by the gauge before admitted air	=·28 cm. of Hg.
Pressure after admitting air	=·91 cm. of Hg.
Vol. of air collected in 154 secs.	=352 c.c.
Atmospheric pressure	=78·5 cms. of Hg.
Cross-section of the tube T	=·41 sq. cm.
Vol. of the air at ·63 cm. pressure entering the tube in 154 secs.	=41070 c.c.
Length of the tube traversed per sec. by the air	=658 cms.
Life of glow	=·03 sec.

Other sets of readings gave values averaging about this, *viz.*, ·03 sec. which is extremely long as compared to the lives of ordinary excited atoms, which has been found by many workers[8] to be of the order of 10^{-8} sec. but is of the same order of the value as obtained by some authors[9] theoretically for the life of metastable atoms. This result therefore points to the conclusion that metastable atoms are probably involved in the phenomenon. This aspect of the matter will be again taken up later.

V

An absorption experiment.

In order to determine the resonance lines of the mercury atoms under the peculiar conditions of the glow it was considered desirable to take the absorption spectrum in the regions available to us, *viz.*, visible and far ultra-violet. Though no positive results are obtained we are briefly describing the condition under which the experiment was performed. The arrangement shown in fig. 4 was used. The glow was

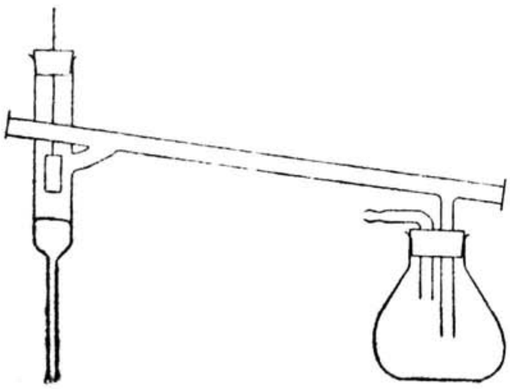

FIG. 4.

allowed to proceed to a side tube about 40 cms. long and kept slightly tilted to avoid the accumulation of mercury.

[8] J. W. Beams, Phys. Rev., Vol. 28, p. 475, 1926.

[9] G. Breit, Phys. Rev., Vol. 29, p. 361.

Two thin clear quartz plates were attached to the ends with sealing wax. As a continuous background a disruptive discharge between two copper electrodes immersed in distilled water was passed and the spectrum was photographed up to 2200 A with a small quartz spectrograph. Though the experiment was performed under excellent conditions, no absorption lines appeared on the plates, and no definite conclusions can therefore be reached. We believe however, it would be worthwhile repeating this experiment in the Schumann region as far as fluorite spectrograph will permit, though the difficulties of observation would be enormous.

VI

Variation of Intensity.

The mercury arc used was the same as used in the absorption experiment, though perhaps it would have been better to have made the tube vertical instead of keeping it only slightly inclined. For it may be pointed out that in spite of the care taken to keep the tube as clean as possible a certain amount of mercury did condense on the tube and obstructed the life of the glow. As soon as a steady state was attained the intensity of the glow at different points of the tube was compared in terms of the illuminating power of a glow lamp. This latter was a small low voltage lamp in front of which was placed a blue coloured glass to match the light with the mercury glow. The photometric comparision of the two lights was carried out with a Lummer and Brodham photometer which was moved parallel to the tube in which the glow was produced. In taking the measurements precautions were adopted to see that no extra light, other than that from the point where the measurements were taken, interfered with the observations, and was therefore completely eliminated. The distance between the tube and photometer was always kept constant, while the distance of the glow lamp was adjusted to attain equality of illumination in the field of view. The results attained are shown graphically in fig. 5. The

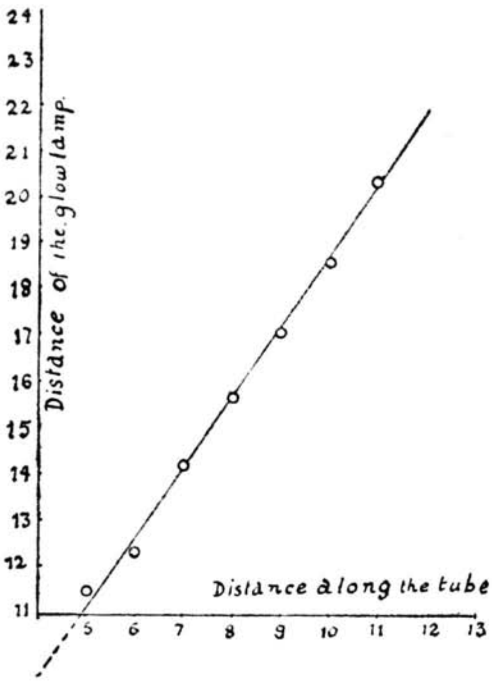

FIG. 5.

different points lie fairly nearly on a straight line and consequently the increase of distances along the tube are proportional to the increase in the distances of the glow lamp. Since the variation of intensity is proportional inversely to the square of the distance, this would indicate that the intensity at different points of the arc, varies inversely as the square of the distance of the point from the arc.

Since the distance of the atoms across any cross-section of the tube from the arc is evidently proportional to the life that these atoms have had, we see from these experiments that the intensity-time curve is also of this form. A simple argument based upon the idea of collisions, then shows that this can be brought only if there are two entities which recombine and release a definite amount of energy which may be taken up by a third body. This relation will hold provided there is a fixed proportion between the number of the two colliding bodies. The rate of recombination must be proportional to the product of the number of ions of each type. Hence,

$$\frac{dn}{dt} \propto n^2$$

$$\text{or } n \propto \frac{1}{t} \text{ and } n^2 \propto \frac{1}{t^2}.$$

$$\text{Since } n^2 \propto \text{I (intensity)}$$

$$\text{we have, I} \propto \frac{1}{t^2}.$$

This is the result actually obtained by experiment.

VII

Discussion.

The experiments described in the foregoing pages clearly point to the positively charged nature of the mercury atoms partaking in the phenomenon, and the evidence for the extraordinarily long life of these atoms is also complete. The present-day tendency is to regard all such atoms in a metastable condition. We may therefore with considerable justification make the tentative suggestion that the afterglow is in some way due to metastable mercury atoms. The question then arises what is the exact energy content of these atoms ? The experiment of Lord Rayleigh cited before on the optical excitation of vapours of different metals on coming in contact with the afterglow mercury, at best provide very uncertain limits, *viz.* 32 and 9 volts. A more satisfactory evidence is available from spectroscopic data. A normal mercury atom has no metastable level but a strong metastable level should be present in mercury atom, which supports the hypothesis made here. The normal condition of the ionised mercury atom is obtained by considering the orientation of the electrons as 10 in O_3 and one in P_1 levels, which gives rise to a $^2S_1$ term as the most fundamental level. In addition, however, a two electron jump, as in the case of copper atom is also possible, giving rise to the electronic configuration 9 O_3 2P_1. From these we obtain $^2D_{2,3}$ terms, which should be inverted, and further should not combine with the deepest $^2S_1$ term, and hence metastable. These predictions on the basis of Hundt's theory of Spectroscopic terms have been recently verified by Paschen [10] who has obtained them in exactly this form. The relevent part of his analysis is given below.

$$10\ O_3\ 1\,P_1 \longrightarrow {}^2S_1 = 151280$$

$$9\ O_3\ 2\,P_1 \begin{cases} \nearrow {}^2D_3 = 115766 \\ \searrow {}^2D_2 = 100728 \end{cases}$$

The energy values of $^2D_3$ and $^2D_2$ are 115766 and 100728 which corresponds to 14·3 and 12·4 volts respectively. Though both of these levels are metastable, probably the atom with which we are dealing is in $^2D_3$ state which is deeper of the two, and this sets a value of 14·8 volts to the energy which can be set free in the afterglow, the ionisation potential of mercury being 10·4 volts. This result is in conformity with the experimental observation of Lord Rayleigh on the interaction of atoms and afterglow. We may point out that on this view the phenomenon of aterglow so far as optical measurements are concerned is essentially a secondary phenomenon, and it has not yet been possible to put forward any evidence to indicate its primary nature. But the possibility of the existence of a primary effect is not excluded. Here we have a three body collision between a metastable

[10] F. Paschen, Berl. Sitzungesber., Dec. 13, 1928.

ionised atom, a neutral atom and an electron which results in the production of an excited and a neutral atom, or alternatively two excited atoms. The very restricted amounts of energy with which these excited atoms are loaded are very probably responsible for the unusually increased intensities of the higher members of principal series of mercury spectrum as observed in the afterglow. The observations on the decay of the intensity of afterglow are consistent with the hypothesis advanced here.

The experiments described above were carried out in the Physics Department of the Government College, Lahore, and the authors express their best thanks to Prof. J. B. Seth and Dr. P. K. Kichlu for the helpful interest they have taken in this work.