THE MEAN LIFE FOR THE MERCURY SPARK SPECTRUM

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Abstract

By using the method previously described by the writer for measuring the average life of excited ions, a mean life of 9×10^{-7} and 8×10^{-7} seconds was found for the 3114 and 2572 lines, respectively, of Hg IV, 6×10^{-7}, 4×10^{-7} and 4×10^{-7} seconds for the 3090, 3312 and 4797 lines respectively of Hg III. The prominent lines of Hg II are estimated to have a mean life of the order of 10^{-8} seconds. These results indicate that the greater the charge of the ion producing the line the longer the mean life. The formula derived for determining the mean life is discussed and experimental results are given which agree quite satisfactorily with the theory developed for measuring the mean life. Intensity-current relations of the spark lines show that they are produced as the result of single electron collisions, which substantiates the assumptions made in the above theory. It is pointed out that lines due to electrons jumping from the same energy level should have the same mean life regardless of the level to which the electrons may jump. The above lines have not been classified so a correlation between the electron transitions and mean lives cannot at present be made.

Discussion of Formula for Determining the Mean Life

Recently the writer[1] has described a new method for determining the life in the excited state which is applicable to lines of the spark spectrum. Electrons in mercury vapor were confined in a beam by a magnetic field. Perpendicular to the beam, an electric field withdrew the positive ions. The light emitted was projected on to the slit of a spectroscope in such a manner that the slit was parallel to the direction of motion of the ions. Several of the spark lines were shown to suffer a displacement along their length and the following formula was derived in order to calculate the mean life $\tau=1/\beta$ after measuring the distance the most intense portion of the line had been shifted,

$$2e^{-\beta(2mx'/Xe)^{1/2}}-e^{-\beta[2m(a+x')/Xe]^{1/2}}-1=0 \tag{9}$$

where X is the cross field, m/e the ratio of mass to charge of the ion and a is one half the width of the beam.

Part 1. The Displacement as a Function of the Mean Life

We shall now consider how the displacement x' will vary with respect to the mean life τ as given by the above equation. Eq. (9) can be written as follows:

$$f(x'\beta)=2e^{-c\beta}-e^{-d\beta}-1=0$$

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[1] L. R. Maxwell, Phys. Rev. **32**, 715–726 (1928).

where $e=(2mx'/Xe)^{1/2}$ and $d=[2m(a+x')/Xe]^{1/2}$. We shall now consider the field X as being constant and determine how x' varies with respect to β. Let us first consider the curve representing the function $f(x'\beta)$ plotted with respect to β holding x' constant and equal to some value greater than zero and less than infinity. For β very great $f(x'\beta)$ will approach -1 and for $\beta=0$, $f(x'\beta)$ will be zero. The slope of the curve is

$$\frac{df(x'\beta)}{d\beta}=de^{-d\beta}-2ce^{-c\beta}=e^{-d\beta}(d-2ce^{(d-c)\beta}) \qquad 10)$$

and for β approaching zero we have

$$\left(\frac{df(x'\beta)}{d\beta}\right)_{\beta\to 0}=d-2c$$

if $d>2c$ then the slope near the origin will be positive and hence the curve will initially rise. Since d is always greater than c, $2ce^{d-c\beta}$ will increase as β increases, making, therefore, the slope of the curve decrease as shown by Eq. (10). As β takes on larger values the slope eventually becomes zero,

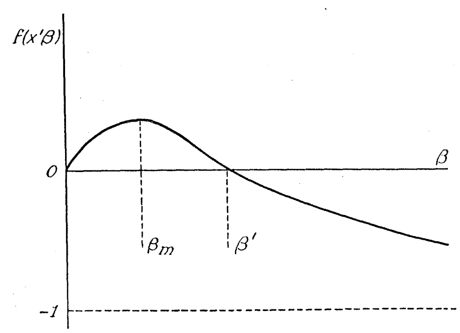


Fig. 1.

and then negative. Thus the curve will reach a maximum and then decrease to negative values for large values of β and for β infinite the curve will approach the value -1. This estimated shape of the curve is illustrated in Fig. 1. The value of β which locates the maximum we shall designate by β_m and it is evaluated by setting the slope given by Eq. (10) equal to zero which gives

$$\beta_m=[1/(d-c)]\log(d/2c). \qquad (11)$$

The point where the curve crosses the axis gives β' the root of the equation, i.e., the value of β which satisfies Eq. (9). We see that β_m will always be less than β'.

If $d<2c$, then the slope will always be negative and the curve will drop from the origin and proceed to the value -1 as β approaches ∞. Similarly, for $d=2c$ the function is negative. For these two cases there exists no root of the Eq. (9) except that for $\beta=0$.

We therefore have shown that in order to obtain β' a solution of Eq. (9) different than zero d must be greater than $2c$. That is

$$\left(\frac{2m}{Xe}(a+x')\right)^{1/2} > 2\left(\frac{2mx'}{Xe}\right)^{1/2}$$

which means that x' must be always less than $a/3$.

Let us now consider how x' varies with β_m. When $x'=0$, i.e. when $c=0$, and $d=(2ma/Xe)^{1/2}$ then $\beta_m=\infty$ as given by Eq. (11). When $x'=a/3$ then $\beta_m=0$. Since it can be shown that $d\beta_m/dx$ is always negative, we then know

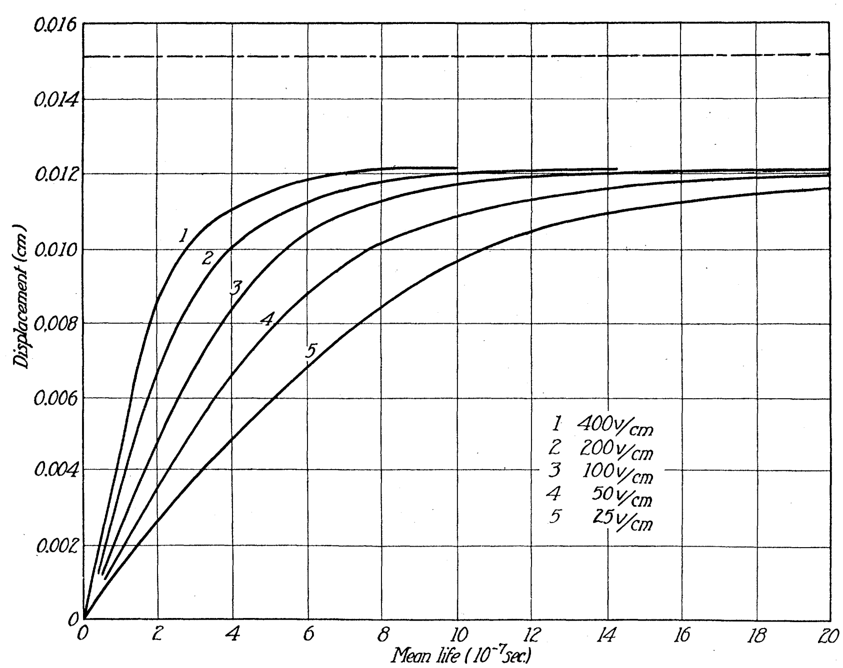


Fig. 2. Relation between the displacement and the mean life for lines of Hg III. Each curve represents results calculated for the particular cross field indicated.

that a curve representing β_m plotted with respect to x' will be a curve without maxima and minima which will extend to infinity at $x'=0$ and cut the abscissae at $x'=a/3$.

It is now easy to obtain x' as a function of β' for we have shown that for $x'=a/3$, $\beta_m=0$, therefore for this value of x', $\beta_m=\beta'$. Let us now choose a β_m very large. Then the corresponding value of x' which satisfies Eq. (11) is very small. But for this value of β_m and x', there exists a $\beta'>\beta_m$ which is a solution of Eq. (9). Therefore, we know the end points of an x', β' curve. It is now necessary to determine if there exist maxima or minima lying between these end points $x'=a/3$, $\beta'=0$ and $x=0$, $\beta'=\infty$. The number of maxima or minima which exist is equal to the number of sets of values x', β' which satisfy Eq. (9) and also the following equation

$$de^{-d\beta}-2ce^{-c\beta}=0 \tag{12}$$

which is obtained by differentiating (9) with respect to β and imposing the condition that $dx'/d\beta=0$. This equation simply specifies which of all those sets of values x', β' that satisfy Eq. (9), will locate a maxima or minima on an x', β' graph. It can be shown that according to these considerations, there is only one maximum and that is at $\beta'=0$, i.e., $x'=a/3$, $\beta'=0$ is the only set of values which fulfill the above conditions. Therefore, we have proved that the curve between the end points has no maxima or minima, and that the largest value of the displacement $(a/3)$ is obtained for $\beta'=0$, or $\tau=\infty$. In Fig. 2 we have x' plotted with respect to the mean life as calculated directly by numerical substitution in Eq. (9) for different cross fields as indicated by the full curves. The horizontal broken line is the limiting value of $a/3$ for the displacements. We see that the displacements approach this value as the mean life is made large.

Part II. The Displacement as a Function of the Cross Field

We shall now consider β to be kept constant and determine how the displacement x' will depend upon the cross field X. We have just shown the relationship between the displacements and the mean life $1/\beta$ for a constant X. The present case is analogous to the above, for here we shall determine how x' depends upon X holding β constant. The relation between x' and

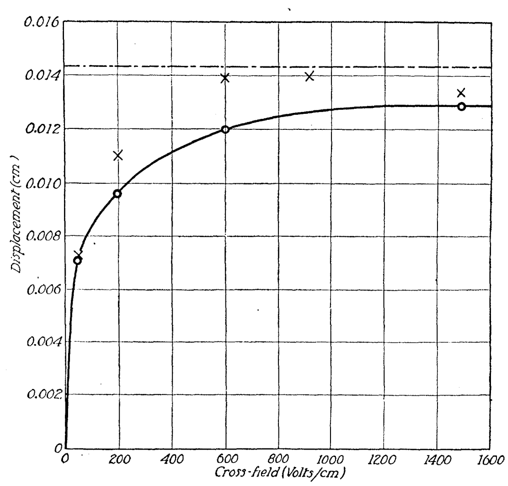


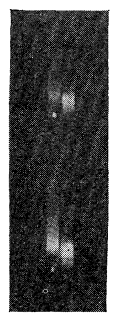
Fig. 3. Relation between the displacement and the cross field for the 4797 line of Hg III. The dots represent the theoretical values of the displacements and the crosses the experimental values.

$X^{1/2}$ will be the same as that found to exist between x' and $1/\beta$ as shown by Eq. (9). Therefore we know that the displacements will never be greater than $a/3$, i.e., $x=a/3$ for $X=\infty$. In Fig. 3 is shown a curve representing x' plotted as a function of X as given by the full line curve. These values are those which were found to satisfy Eq. (9) by direct numerical substitution and hence give the theoretical prediction of how the displacements depend upon the field. The horizontal broken line gives the limiting value of $a/3$ for the displacements. It is noticed that the curve approaches this value asymptotically as the field becomes large.

Experimental Arrangement and Results

The apparatus used in the present work was the same as that previously described except that it was designed to accommodate greater cross fields. This was accomplished by placing the tube between the pole pieces of an electro-magnet which produced a magnetic field of 2500 gauss and hence permitted large values of the cross field to be used without disturbing the electron beam. The new apparatus was considerably smaller but the essential parts of it were the same as in the former tube. The same type of filament and similar placement of the side plates were used. The shape of the electron beam is determined by the shape of the filament. The filament was a straight wire which caused the beam to be of a ribbon-like character. The electrode S_2 was omitted and a Faraday cage of one centimeter depth was used in place of the long cage C. Inside the Faraday cylinder a non-uniform cross field was used to prevent the return of secondary electrons into the region photographed.

600 volts/cm



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200 volts/cm

Fig. 4. A reproduction of a portion of two typical plates showing the displaced 4797 line of Hg III indicated by the dot and the undisplaced 4916 Hg arc line. The direction of motion of the ions is indicated by the arrow. The cross field applied for the upper photograph was 600 volts/cm while for the lower 200 volts/cm was used.

Figure 4 is a reproduction of a portion of one of the spectrum plates. The ions were moving in the direction indicated by the arrow. The slit of the spectrograph was purposely made very wide so that the lines would be of sufficient width to allow intensity measurements along their length. The line indicated by the dot is the 4797 of Hg III and the other is the 4916 line of the mercury arc spectrum. It can be easily seen that the spark line is distorted and the line actually pulled up in the direction of motion of the ions. The arc line is of course not affected by the field. In the upper set of lines the cross-field was 600 volts/cm while in the lower, the field was 200 volts/cm. Photographs were also taken with this spark line for other fields and the results are given in Fig. 3. The actual displacements were measured and are indicated by the crosses. The full line curve located by the dots gives the theoretical values as mentioned above. The value of the mean life is taken to be 4×10^{-7} sec. We see that the agreement between the experimental results and the theory is quite satisfactory.

The accuracy with which the mean life can be measured depends greatly upon the value of the cross field. For example, suppose we were to examine a line which had a mean life of 1×10^{-6} sec and were to use a cross field of 400 volts/cm. We see from Fig. 2 that the displacement which we would measure would lie on the curve at a point where the slope was about zero. Therefore, any small error in the measurement of the displacement would produce a very great error in the determination of the mean life. We see from the figure that a choice of a field of 25 volts/cm would give a decidedly more accurate measurement of the mean life. In general the value of the field should be so adjusted that the point representing a displacement corresponding to a certain mean life lies on that part of the curve where the slope is the greatest.

The results obtained for the mean life for the lines of the mercury spark spectrum are presented in Table I. The mean life for the 3832 line of Hg IV

TABLE I. *Mean life of various spark lines of mercury.*

Wave-length (A)	Type of spectrum	Mean life (sec.)
3090	Hg III (E_2)	6×10^{-7}
3312	Hg III (E_2)	4×10^{-7}
4797	Hg III (E_2)	4×10^{-7}
3114	Hg IV (E_3)	9×10^{-7}
2572	Hg IV (E_3)	8×10^{-7}

was estimated to be of the same order of magnitude as those given in the table. The prominent lines of the first spark spectrum of mercury such as the 2848, 2947, 3208, 3708 and many others did not exhibit any appreciable displacement so that their mean life could not be measured. A mean life of 10^{-8} seconds would produce a very small displacement as illustrated in Fig. 2 for lines of the Hg III spectrum while for the Hg II spectrum the displacements would be still less. Thus we see that it is impossible (for the cross field used) to measure mean lives of 10^{-8} seconds for the Hg II spectrum. Therefore these undisplaced spark lines of Hg II probably have a mean life of that order of magnitude. The lines 2262 and 2916 of Hg II did show a noticeable displacement in the case of high cross fields, but the mean life for these lines has not been measured. However, we conclude that in general the mean life for the first spark spectrum is of the order of 10^{-8} seconds. For the second and third spark spectra, the life is considerably greater, while the lines of Hg IV show slightly higher mean lives than do the lines of Hg III. These results indicate that the greater the ionic charge the longer the life in the excited state.

It has been assumed in this method of calculating the mean life that the line is produced as a result of a single electron collision, i.e., the atom is multiply ionized and excited at the moment of collision of the atom and electron. Since the concentration of positive ions is small, the probability of collision between electrons and unexcited ions is so small that the number of excited ions formed as a result of this double collision process would not be great enough to produce any light. The pressure of the mercury vapor in the tube was about 0.001 mm so that the total ion current was of the order of 10^{-5} amperes which necessitates that the ion concentration be small. Valasek[2] has shown that many of the spark lines of mercury formed under similar conditions were produced as the result of single collisions. This conclusion was arrived at after he found that the intensity of the spark lines was directly proportional to the exciting electron current. In fact, Valasek found no lines due to multiple collisions. In the present work similar intensity-current relations were measured for the 3208 of Hg II, 3090 and 3312 of Hg III, 3114, 2572 of Hg IV and the relationships were found to be linear. All of the measurements of this character show that the mercury spark lines are the result of single collisions which substantiates the assumptions that have been made in the above calculations.

The value of the charge of the ion responsible for the lines quoted in the above table was obtained from the results of L. and E. Bloch,[3] who, by means of an electrodeless discharge tube, have classified a large number of the spark lines of mercury into either the first, second or third spark spectrum. From Eq. (9) we see that in order to calculate the mean life, it is necessary to know e the total charge of the ion; and any error in e which might arise in the measurements of L. and E. Bloch will alter the value of the mean life given in Table I. On the other hand, if we knew the mean life for the spark line it would be possible to measure, by the present method, the charge of the ion producing the line.

Discussion of Results

Let us be concerned with determining how the mean life should depend upon the electron transitions. If N be the number of atoms which at any time t have an electron in a certain excited state designated by the quantum numbers nk; and if $A_{nk}^{n'k'}$ be the probability of transition from the state nk to state $n'k'$, then the number of electrons which will leave state nk and go to $n'k'$ in time dt is given by

$$-dN_{nk}^{n'k'} = A_{nk}^{n'k'} N dt$$

Thus the total number of electrons which will leave the state nk per unit time, is

$$\frac{-dN}{dt} = \sum_{n'k'} -dN_{nk}^{n'k'} = \sum_{n'k'} A_{nk}^{n'k'} N$$

where the summation is to be extended over all the possible states to which the electron can jump. Therefore, the population N of the nk level at any time t is given by

[2] Joseph Valasek, J.O.S.A. **17**, 102 (1928).
[3] L. and E. Bloch, Jour. d. Physique **4**, 333 (1923).

$$N = N_0 \exp -\left[\left(\sum_{n'k'} A_{nk}^{n'k'}\right) t\right]$$

where N_0 is the number of atoms with an electron in the nk state at the time $t = 0$.

The energy emitted per unit time at time t by the jumping of electrons from state nk to $n'k'$ is $A_{nk}^{n'k'} h\nu_{nk}^{n'k'} N$, where $\nu_{n'k}^{n'k'}$ is the frequency of the emitted light. Therefore, the intensity of the spectral line is given by the following after replacing N by its value from the above equation,

$$I_{nk}^{n'k'} = A_{nk}^{n'k'} h\nu_{nk}^{n'k'} N_0 \exp -\left[\left(\sum_{n'k'} A_{nk}^{n'k'}\right) t\right] \tag{13}$$

The average life τ of the excited state nk is given by

$$\tau = \left(\sum_{n'k'} A_{nk}^{n'k'}\right)^{-1}$$

We see from this equation that all of those lines due to electrons jumping from the same level should give the same value for the mean life. This simply means that the life of an excited state can be measured by using any line which originates from that particular level. The intensity of the lines, however, will depend upon the value of $A_{nk}^{n'k'}$ as shown by Eq. (13).

Since the lines given in the above table have not been classified as to their electron transitions it is not possible at present to correlate the above results for the mean lives with the electron jumps. The two lines 3312 and 4797 of Hg III, however, have the same mean life so that we conclude that they must originate from the same energy level.

Kerschbaum[4] has determined the mean life of a number of lines employing the canal ray method of Wien. He has found in general that not only those lines starting from a particular level give the same mean life but all of the arc lines of a given element have the same mean life. Since we have shown above that the mean life is equal to the reciprocal of the sum of the transition probabilities for all possible jumps from the level concerned it is not to be expected that the mean life should be the same for all of the levels of the atom, as Kerschbaum's results seem to indicate. For the spark lines of singly ionized barium, he found that the two lines 4554 and 4934 which originate from the same level (i.e. two lines of the principal series of Ba^+) gave different mean lives, 2.7×10^{-8} and 1.2×10^{-8} sec, respectively. This result is not in agreement with the above considerations.

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[4] H. Kerschbaum, Ann. d. Physik **83**, 287 (1927).

600 volts/cm

200 volts/cm

Fig. 4. A reproduction of a portion of two typical plates showing the displaced 4797 line of Hg III indicated by the dot and the undisplaced 4916 Hg arc line. The direction of motion of the ions is indicated by the arrow. The cross field applied for the upper photograph was 600 volts/cm while for the lower 200 volts/cm was used.