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PROBE AND RADIATION MEASUREMENTS IN THE COPPER ARC.*

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Abstract. The Langmuir probe has been used to explore the copper arc. The cathode fall of the normal arc has been found to be 20.5 volts, which equals the second ionization potential of copper Cu (II), while the cathode fall for the hissing arc has been found to be 14.0 volts. The potential gradient along the arc stream is constant and therefore the space charge is zero and the concentrations of positive ions and electrons are equal. The average energy of the electrons throughout the arc is between 2.1 and 2.7 volts. The space potential, when measured with reference to the cathode, depends on the current flowing in the arc in the same way as the over all potential, i.e., $V = A + \frac{B}{I^n}$ where A, B, and n are constants. The positive ion concentration in the arc stream increases as the arc current increases according to the equation $n_+ = b\epsilon^{aI}$ where a and b are constants. The light per unit volume has been measured for twelve copper arc spectrum lines and found to

* Presented to the Graduate Committee of Purdue University as the thesis for the graduate degree of Electrical Engineer.

follow the same sort of equation as above, i.e., $l = c\epsilon^{paI}$, where c is a constant, a the constant appearing above, and p takes on values 2, 3, 4, etc. Eliminating the current between these two equations, it is shown that the light intensities in lines λ3248, λ3274, and λ5105 of the copper arc are proportional to the *square* of the electron concentration while the intensities of λ2618 and others are proportional to the *cube* of the concentration, etc. Thus it is demonstrated that the relative intensities of the lines in the arc spectrum are not fixed but depend in a definite manner on the arc current flowing since the excitation is produced as a result of the cumulative action of the electrons in which 2, 3, 4 or more electrons take part.

INTRODUCTION.

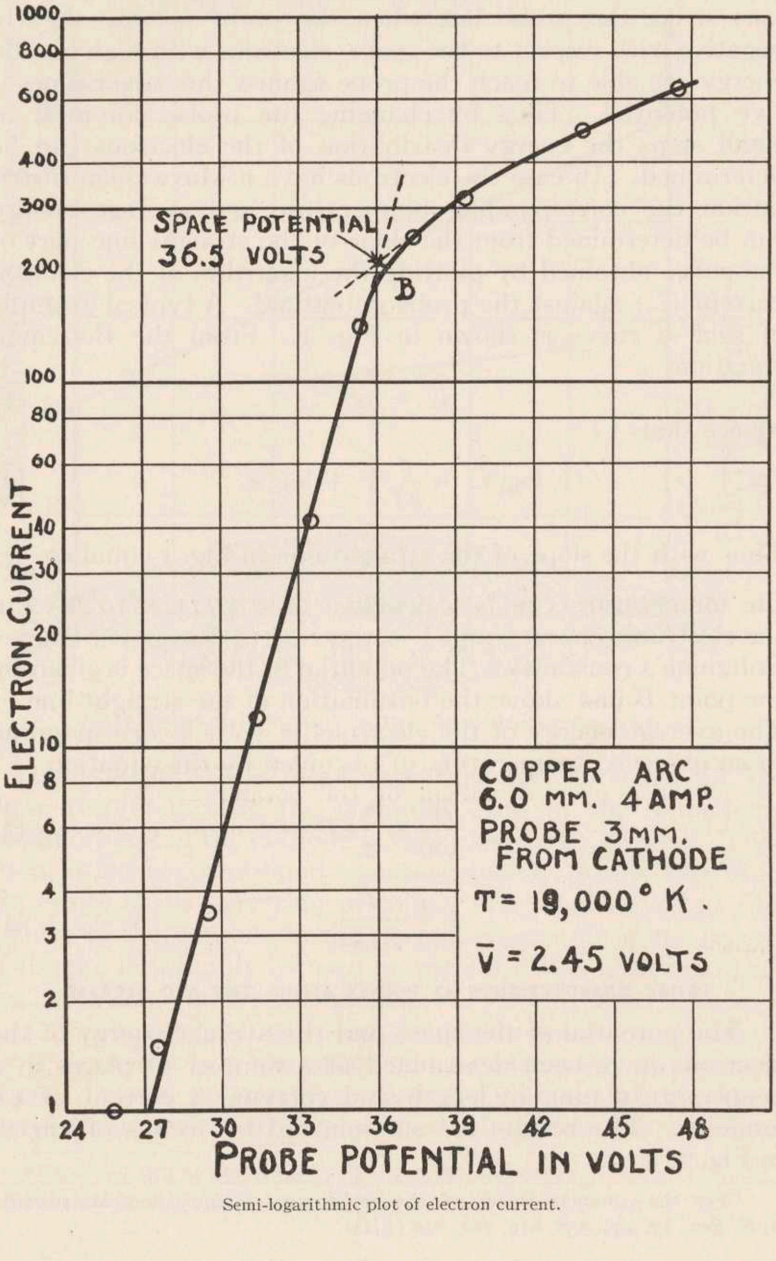
In a recent issue of this JOURNAL, a report was made on the use of the Langmuir probe for the study of the normal electric arc.[1] Those methods have been used to study the normal arc between copper electrodes in order to find (1) the average energy of the electrons in this arc; (2) the distribution of potential along the arc stream; and (3) the positive ion concentration in the central portion of the arc with different currents flowing. A method was worked out by which the variation in the intensity of certain of the lines of the copper spectrum could be measured when the arc current was changed. These results combined with those of the probe measurements have revealed many interesting facts concerning the detailed mechanism of the copper arc which may possibly be common to other arcs between metals at atmospheric pressure.

PROBE MEASUREMENTS.

The experimental procedure may be recalled to mind as follows: a copper wire probe 0.01 inch in diameter is moved through the arc stream at practically a constant velocity of about 60 cm. per second, while the potential of this probe is maintained at a definite value with reference to the negative electrode by means of a low resistance battery. The current which flows through the probe circuit during the passage of the probe through the arc stream is registered on a ballistic galvanometer. When the probe is very negative with respect

[1] JOURNAL OF THE FRANKLIN INSTITUTE, **206**, 43 (1928).

FIG. 1.



Semi-logarithmic plot of electron current.

to the space in the arc through which it travels only positive ions strike the probe but when the probe is only slightly negative with respect to the space, electrons with high kinetic energy are able to reach the probe against this adverse negative potential. Thus by changing the probe potential in small steps the energy distribution of the electrons can be determined. In case the electrons have a Maxwellian distribution the corresponding temperature and average energy can be determined from the slope of the straight line part of the curve obtained by plotting the logarithm of the electron current (i_-) against the probe potential.[2] A typical example of such a curve is shown in Fig. 1. From the Boltzman equation

$$i_- = a\epsilon^{eV/kT} \tag{1}$$

we see that

$$\log_\epsilon i_- = \frac{e}{kT} V + \log_\epsilon a. \tag{2}$$

Thus with the slope of the straight line in Fig. 1 equal to $\frac{e}{kT}$, the temperature can be calculated ($e = 4.774 \times 10^{-10}$ e.s.u. the electronic charge; and $k = 1.372 \times 10^{-16}$ ergs per degree, Boltzman's constant). The potential of the space is given by the point B just above the termination of the straight line. The average energy of the electrons in volts $\bar{v}$ corresponding to an observed temperature (T) is given by the equation

$$\frac{e\bar{v}}{300} = \frac{3}{2} kT, \tag{3}$$

$$\bar{v} = \frac{T}{7{,}732}. \tag{4}$$

PROBE MEASUREMENTS AT POINTS ALONG THE ARC STREAM.

The potential of the space and the average energy of the electrons have been determined at a number of places in a copper arc 6 mm. in length and carrying a current of 4.0 amperes. The results are summarized by means of curves in Fig. 2.

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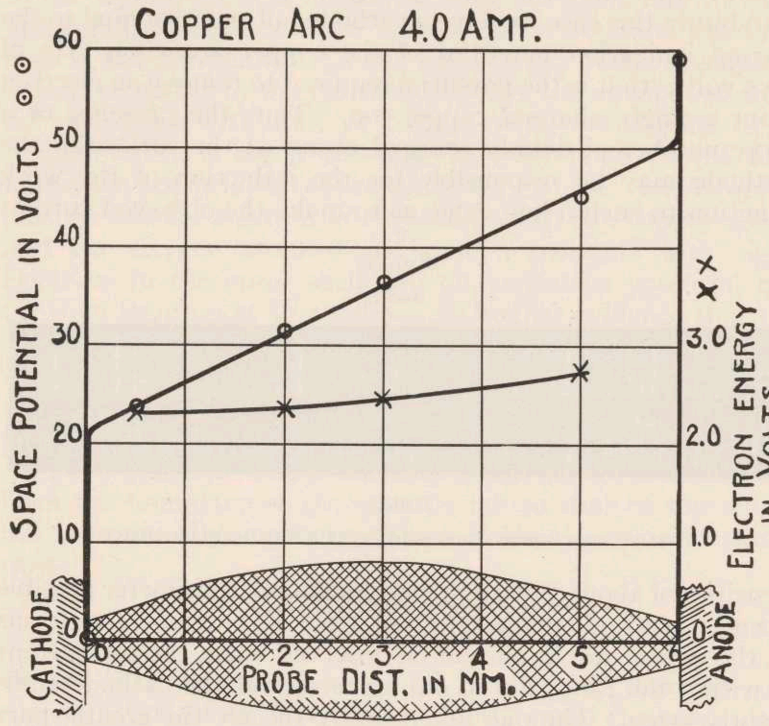
[2] For the complete theory of the probe see Langmuir and Mott-Smith, *G. E. Rev.*, **27**, 449, 538, 616, 762, 810 (1924).

FIG. 2.



Distribution of potential and electronic energy along the copper arc.

Cathode fall: The most important fact brought out by these results is that the potential drop in the immediate neighborhood of the cathode is very close to 20.5 volts. This observation is corrobrated spectroscopically by the fact that the entire spark spectrum of copper can be observed at the surface of the cathode in the normal copper arc if the image of the arc is carefully focused on the slit of the spectroscope.[3] Fig. 3 serves to prove this point.

Over the range of wave-length λ2330 to λ2850 every one of the 35 lines listed by Shenstone[4] can be seen easily on the negative. In arcs previously studied, the cathode fall has been found to be practically equal to the ionization potential of

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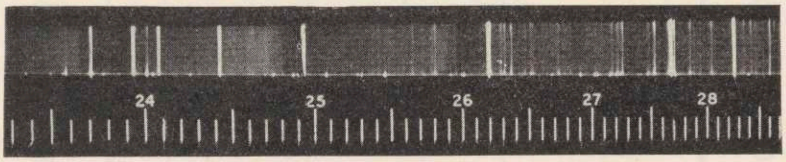
[3] Observed also by Hagenbach, *Phy. Zs.*, **12**, 1015 (1911).

[4] Shenstone, *Phys. Rev.*, **29**, 380 (1927).

the electrode material (the cyanogen molecule for the carbon arc) but in this case we have a cathode fall exactly equal to the second ionization potential of the copper atom Cu (II) of 20.5 volts,[4] that is the potential required to remove an electron from a singly charged copper ion. Thus the presence of a large number of doubly charged atoms at the surface of the cathode may be responsible for the reduction of the work function to such a low value as to make the observed current

FIG. 3.

Anode



Cathode

Spectrum plate showing copper spark lines at the surface of the cathode.

densities of about 3,000 amperes per square centimeter possible even at a cathode temperature of 2500° K. or less. Two forms of the copper arc in air can be observed when the arc current is within the range 2.0 to 8.0 amperes and the cathode sufficiently large. The one taken on by the arc the greater part of the time has been considered as the "normal" arc and is the one which has received the greater attention. The second form, some times called the "hissing arc," is characterized by greater luminosity in the core and also in the red flame sheath which surrounds the arc while the over all voltage between the electrodes is 7.0 to 8.0 volts less than that required to operate the "normal" arc. If the cathode is only two or three millimeters in diameter the hissing arc is usually the only form found. The fact that the greater part of this change in voltage takes place in the cathode fall has been demonstrated by probe measurements made by Hagenbach [2] in which a high resistance voltmeter was used to measure the potential of a probe immersed in the discharge. Langmuir has shown that the voltmeter does not show the potential of the space but shows the potential at which equal numbers of positive and negative ions reach the probe. The cathode fall in the hissing arc was measured using the Langmuir method and found to be about 14.0 volts which is 6.5 volts less than that in the normal arc. If the cathode fall in the hissing arc is to correspond to the ionization of the active vapor it must be associated with that of copper oxide or cuprous oxide (Cu_2O) for it is much too high to correspond to the first ionization potential of copper which is 7.7 volts. Since copper has one valence electron in this compound, two copper atoms and one oxygen atom should give a molecule with eight electrons in the outer shell and an ionization potential not far from krypton at 13.3 volts. As further evidence that the cathode fall of the hissing arc is to be associated with the oxide we can take Hagenbach's observation that only the normal form of the arc can be produced in an atmosphere of nitrogen using clean copper electrodes.[5]

The arc stream: The potential gradient along the arc stream from the boundary of the cathode fall to that of the anode fall is practically constant. Since Poisson's equation states that

$$\frac{d^2V}{dx^2} = -4\pi\rho, \qquad (5)$$

we see that the space charge (ρ) is zero and therefore the concentration of electrons must exactly equal the concentration of positive ions. The total current flowing along the arc stream is the sum of the electron current (I_-) and the positive ion current (I_+) and these stand in the ratio

$$\frac{I_-}{I_+} = \frac{v_-}{v_+}, \qquad (6)$$

where v_- and v_+ are the corresponding ion velocities in a field of 47 volts per cm.

Anode fall: The anode fall is between 7 and 8 volts. The factors which serve to determine its value are not immediately obvious.

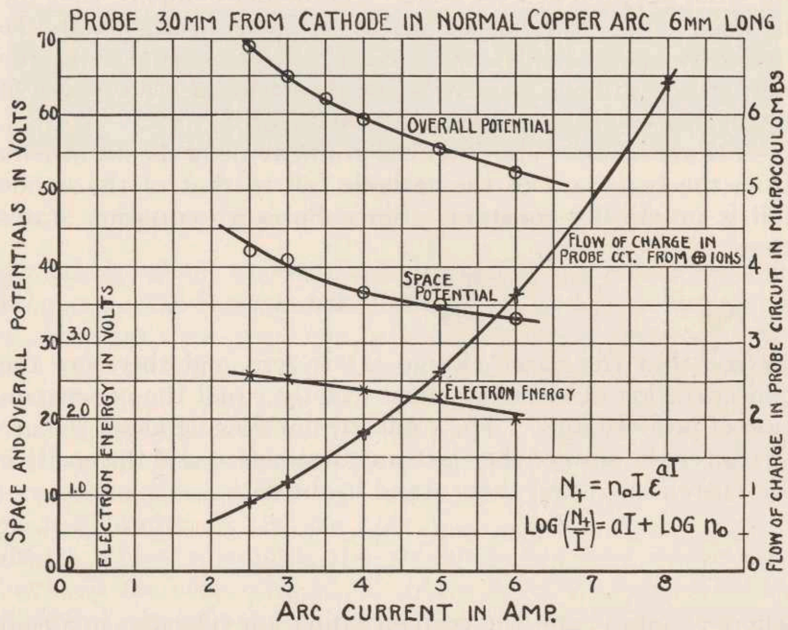
Electron energy: The average energy of the electrons increase slightly as they proceed from the cathode to the anode. These energies are 2.3 ± 0.1 volts near the cathode and 2.7 ± 0.1 volts near the anode.

[5] Hagenbach & Veillon, *Phy. Zs.*, 11, 833 (1910).

COMPARISON OF PROBE MEASUREMENTS IN ARCS CARRYING DIFFERENT CURRENTS.

Copper arcs 6.0 mm. in length and carrying currents ranging from 2.5 to 6.0 amperes were studied with a copper probe moved through the arc stream at a distance of 3.0 mm. from the cathode. The average electron energy, the space potential, and a measure of the positive ion current to the probe were determined in each arc. These results are shown by the different curves of Fig. 4.

FIG. 4.



Probe measurements in the copper arc with the probe half way between the electrodes.

Space potential: The space potential at the point half way between the electrodes follows the same form of function in its dependence on the arc current as the over all potential and is given by the equation

$$V = A + \frac{B}{I^n}. \qquad (7)$$

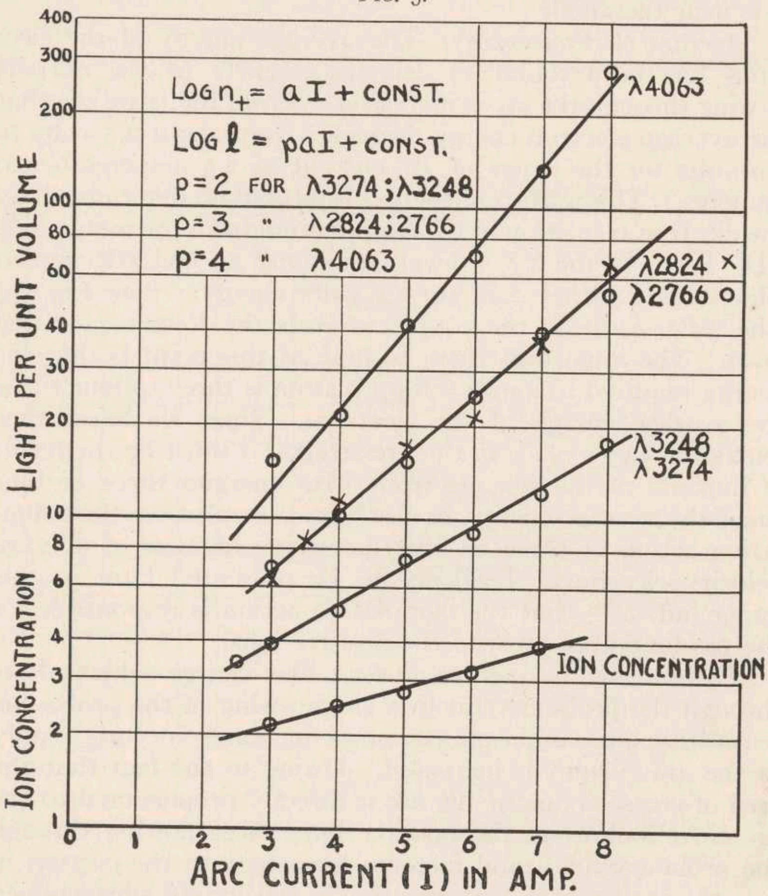
The corresponding values for the constants are $A = 20$,

$B = 41$, and $n = 0.64$ for the space potential while $A = 36.3$, $B = 59$, and $n = 0.67$ for the over all potential. Since in general the value of n depends upon the absolute temperature, the lower value of n of 0.64 may result from the fact that the average temperature of the arc is lower near the cathode than it is near the anode.

Average electron energy: The average energy of the electrons has been found to decrease slightly as the current flowing through the arc is increased. From Fig. 4 we see that the average electron energy decreases from about 2.5 volts to 2.0 volts for the range of arc current of 2.5 amperes to 6.0 amperes. This electron energy is probably determined by the electron transition in the copper atom from the metastable "D" levels to the $2^2P_{1,2}$ levels involving an inelastic impact which takes either 2.14 or 2.4 volts energy. (See Fig. 6.) The $2^2P_{1,2}$ state in the copper atom is the lowest radiating level. The important thing to note at this point is that the energy required to ionize a copper atom is three to four times the average energy of the electrons. Since we know that ionization takes place in the arc stream, it must be the result of impacts of the few electrons with energies three or four times the average energy, or else it must result from the cumulative action of three or four successive impacts of average velocity electrons. Evidence to be presented later in this paper indicates that the cumulative action is responsible for the production of most of the positive ions.

Positive ion current to probe: The charge which flows through the probe curcuit in a single swing of the probe due to positive ions coming to the probe increases very noticeably as the arc current is increased. Owing to the fact that the area of cross-section of the arc is directly proportional to the arc current flowing, the positive ion charge flowing through the probe circuit would increase linearly with the current in case the positive ion concentration in the arc stream remained unchanged. The fact that this curve is convex toward the current axis (see Fig. 4), shows that the concentration of positive ions increases as the arc current is increased. The ordinates plotted show the positive ion charge flowing through the probe circuit when at the potential of the space. This is obtained by extrapolating the "voltage-current" curve observed over a range of voltage which is so negative with respect to the space that the electron current is too small to measure. The positive ion probe current, which is a measure of the number of positive ions which strike it and give up

Fig. 5.



Curves showing dependence of light and ion concentrations on arc current in copper arc.

their charges, can be represented by the simple empirical equation

$$N_+ = n_0 I \epsilon^{aI}, \tag{8}$$

in which n_0 and a are constants. The charge which flows through the probe circuit when the probe passes through the arc stream of radius r at a constant velocity v can be shown to be given by the equation

$$N_{+} = \frac{\pi r^2 i_{+}}{v}, \tag{9}$$

where i_{+} is the current to the probe per unit length. Since the motion due to thermal agitation is large compared to that due to the drift in the direction of the field, the current i_{+} is proportional to the positive ion concentration n_{+}. From equations (8) and (9) and the fact that the area of the arc is proportional to the current flowing, we can express the relation between the positive ion concentration and the arc current by equation (10).

$$n_{+} = b\epsilon^{aI}. \tag{10}$$

Here a and b are constants and n_{+} is proportional to $\frac{N_{+}}{I}$. Graphically this relationship is shown by the straight line of Fig. 5 designated "ion concentration." Since

$$\log_{\epsilon} n_{+} = aI + \log_{\epsilon} b, \tag{11}$$

the value of a is given by the slope of this straight line.

INTENSITY OF SPECTRAL LINES AS A FUNCTION OF ARC CURRENT.

Method of measurement: In order to determine how the intensity of certain spectral lines in the copper arc depends on the current flowing in the arc, it is necessary to have a device whose response is proportional to the light intensity falling on it. The light from the arc was passed through a quartz lens and two quartz right angle prisms adjusted to form an image of the arc on the slit of a D 41 Hilger monochromatic illuminator. The axis of the image was turned into the horizontal position by prisms so that the light which passed through the monochromatic illuminator all came from the small cylinder in the arc syream bounded by two planes passed perpendicular to the axis of the arc and separated by a distance equal to the width of the slit of the monochromator. The arc was so adjusted that this cylinder occupied the samc region which was swept through by the probe when it was set to swing through half way between the electrodes. The light intensity for the lines between λ4023 and λ5220 was measured by a potassium-hydride photoelectric cell made in our laboratory [6] coupled with a vacuum tube amplifier with a sensitivity of 24,000 mm. per volt and an input resistance of about 2,000 megohms. To measure the light intensity in the ultraviolet from λ2441 to λ3274, the light was made to fall on a glass container with a quartz window and filled with a saturated solution of esculin in water. A part of the fluorescent light produced by the ultraviolet passed into the photoelectric cell and gave a current which could easily be measured. The fact that the fluorescence is proportional to the intensity of the ultraviolet light falling on the container was proved by measuring the change in photoelectric current when the intensity of the ultraviolet light was reduced by interposing various wire screens at the lens. The absorbing power of the screens measured with blue light was found to be the same as that for the ultraviolet assuming the intensity of fluorescence proportional to the incident ultraviolet radiation.

Experimental results: The first lines to be examined were the two resonance lines λ3274 and λ3248 which correspond to the $1^2S - 2^2P_{1,2}$ transitions. Although these two lines could not be definitely resolved, no harm should result since they correspond to transitions so similar in all respects. The results of these measurements showed that the light intensity L followed the same simple empirical relationship found for the positive ion current and given by equation (8). This equation in more suitable terms is given in equation (12)

$$L = l_0 I \epsilon^{2aI}. \tag{12}$$

Here the arc current is I, and l_0 and a are constants. Since a negligible part of the radiation of this wave-length originating throughout the volume of the arc is absorbed in the arc, we can take the light per unit volume l as being proportional to $\frac{L}{I}$ and write equations (13) and (14).

$$l = c\epsilon^{2aI}, \tag{13}$$

[6] "Instruction on the Making of Potassium-hydride Photoelectric Cells," W. B. Nottingham, JOURNAL OF THE FRANKLIN INSTITUTE, **206**, 637 (1928).

$$\log_e l = 2aI + \log_e c. \tag{14}$$

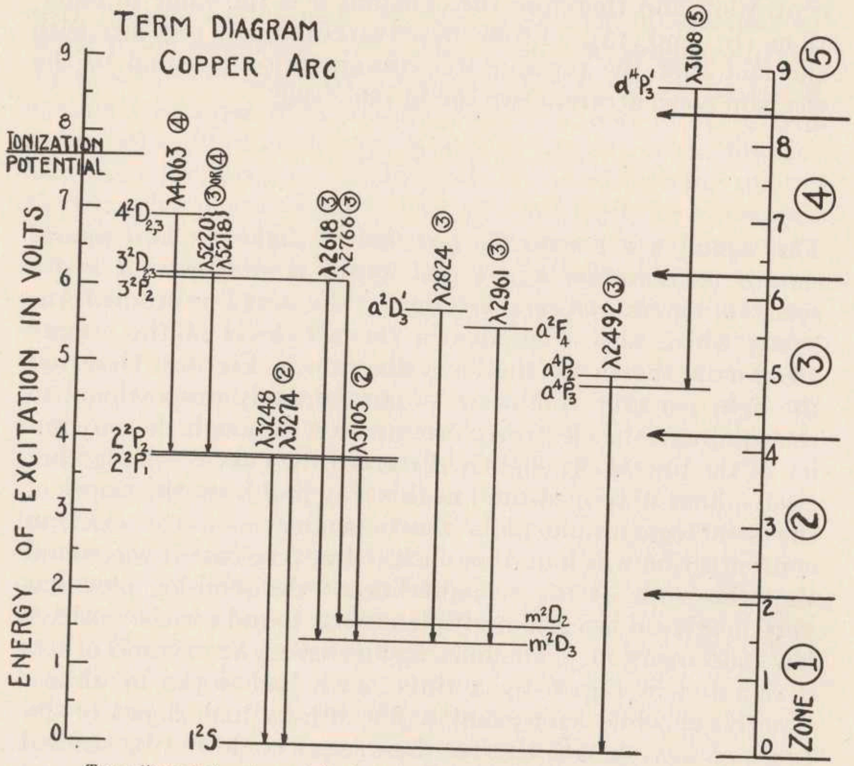
From Fig. 5, we see that the slope of the straight line designated "λ3274; λ3248" is twice that for the positive ion concentration and therefore the constant a is the same in equations (10) and (13). From these two equations, together with the fact that the positive ion concentration is equal to the electron concentration, we see at once that

$$l = \frac{b^2}{c} n_-^2. \tag{15}$$

This equation expresses the fact that the light per unit volume emitted as radiation λ3274 and λ3248 is proportional to the square of the electron concentration. The next line studied was λ5105 which also originates in the 2^2P level of the copper atom as is shown by the level diagram in Fig. 6. Here too the light per unit volume was approximately proportional to the square of the electron concentration although the proximity of the line λ5153 slightly distorted the curve. Altogether twelve lines were measured in this way and from the slopes of the semi-logarithmic plots the dependence on the electron concentration was found for each. In every case it was found that the slope of the straight line of the semi-log plot was very nearly an integral multiple of that found for the positive ion concentration. The lines λ2961, λ2824, λ2766, and others designated in Fig. 6 by a three, each had slopes of almost exactly $3a$ while λ4063 and a few others had slopes of $4a$. Lines of wave-length shorter than λ2441 could not be studied because here the absorption of the light in the hot gas around the arc can not be neglected. Intensity measurements at λ2392 and λ2293 showed very little change when the arc current was changed as a result of this increased absorption.

Interpretation of results: These results can be easily explained if we assume that cumulative impacts of electrons on atoms are largely responsible for the excitation of the atoms. Let us imagine that there are certain discrete excitation energy levels in the atoms making up the gas of our arc discharge and designate these by 0, 1, 2, 3, etc. Let the difference in energy between consecutive states equal the average energy of the electrons. Assume that state "0" is the normal unexcited state and that state "1" can be produced by a single impact of an electron with an energy equal to the average

FIG. 6.



Term diagram showing certain of the levels and lines of the copper arc spectrum.

energy of all the electrons. Within a unit volume the rate at which atoms enter or leave state "1" will be given

$$\frac{dN_1}{dt} = a_{01}N_0n - b_1N_1 - c_{12}N_1n. \qquad (16)$$

Here N_1 is the number of atoms per unit volume in state "1," n is the concentration of electrons, a_{01} is the constant of proportionality which when multiplied by N_0, the concentration of unexcited atoms, and n gives the rate at which atoms are excited to the state "1." The term $-b_1N_1$ represents the rate at which atoms leave state "1" by a spontaneous giving up of energy in radiation. The term $-c_{12}N_1n$ gives the rate at which atoms leave state "1" to enter state "2" as a result of impacts with electrons. This rate certainly must be proportional to the concentrations N_1 and n with c_{12} as the constant of proportionality. In the steady state we must have $\frac{dN_1}{dt} = 0$ and therefore we can write

$$a_{01}N_0n - b_1N_1 - c_{12}N_1n = 0 \tag{17}$$

and in the same way we can write

$$c_{12}N_1n - b_2N_2 - c_{23}N_2n = 0, \tag{18}$$

$$c_{23}N_2n - b_3N_3 - c_{34}N_3n = 0. \tag{19}$$

These equations can be solved for N_1, N_2, etc., and we find

$$N_1 = \frac{a_{01}N_0}{b_1 + c_{12}n}\,n, \tag{20}$$

$$N_2 = \frac{a_{01}N_0c_{12}}{(b_1 + c_{12}n)(b_2 + c_{23}n)}\,n^2, \tag{21}$$

$$N_3 = \frac{a_{01}N_0c_{12}c_{23}}{(b_1 + c_{12}n)(b_2 + c_{23}n)(b_3 + c_{34}n)}\,n^3. \tag{22}$$

From these equations we see that the number of atoms in state "1" is proportional to the concentration of electrons; the number in state "2" is proportional to n^2 etc., if the number of atoms which leave a given state by radiating energy is large compared with those which leave it to enter a higher state due to electron impacts. We should therefore expect the intensity of light per unit volume which is given off the arc stream to be proportional to the square of the electron concentration if the atoms are each excited as result of two impacts of electrons. This theory is supported by the fact that the level diagram of Fig. 6 can be divided into "zones." Lines resulting from transitions originating in the second zone have intensities proportional to the square of the electron concentration, while those from the third zone are proportional to the cube of the concentration and so on. It is important to note that the width of these zones, measured in volts, is about 2.1 volts and the average energy of the electrons as given by the probe measurements is also slightly greater than 2.1 volts. (See Fig. 4.)

GENERAL CONCLUSIONS.

These experiments have brought out a few simple facts concerning the mechanism of the electric arc which may be worth reviewing. The cathode fall in potential is usually equal to the ionization potential of the active gas but may, as in the case of the normal copper arc, be equal to the potential required to remove the second electron from an atom already singly ionized. The presence of a large concentration of singly or doubly charged atoms in the immediate neighborhood of the cathode surface is no doubt partly responsible for the high current density at the cathode. The electrons are found to have approximately a Maxwellian distribution of velocity with an average energy determined by critical potentials of the atom in case the gas or vapor playing the controlling part is monatomic. In case the gas is diatomic, as in the carbon arc in which we have the cyanogen molecule, the average energy of the electrons is not determined sharply and is not constant along the arc stream. This accounts for the "striations" found in the carbon arc.[1] The electrons produce the excitation responsible for the emission of light as a result of the cumulative action of successive impacts of electrons on atoms. It follows from this that the relative intensities of the lines observed in an electric arc are not fixed but depend on the current flowing because the concentration of electrons is a function of the current.

It is with pleasure that I acknowledge my indebtedness to Dr. W. F. G. Swann for many valuable suggestions.

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