In the case of restricted relativity theory we have

$$u = \frac{cE}{\sqrt{(E-V)^2 - m^2c^4}}; \quad v = c\sqrt{1 - \frac{m^2c^4}{(E-V)^2}}$$

where c is the velocity of light. The same reasoning as above leads to the same result. Epstein[6] has just published a paper which leads to the relation $E = h\nu$ along somewhat different lines.

[1] Goursat, E., *Cours d'Analyse*, Tome, **3**, Chap. 25.

[2] *Ann. Physik*, **81**, p. 133, 1926.

[3] Schrödinger, E., *Ibid.*, **79**, p. 489, 1926.

[4] Loc. cit., p. 500ff.

[5] de Broglie, L., Theses, Paris, 1924; *Ann. physique* (10), **3**, p. 38, 1925.

[6] Epstein, P., these PROCEEDINGS, **13**, 94, 1927.

HEATS OF CONDENSATION OF POSITIVE IONS AND THE MECHANISM OF THE MERCURY ARC

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The two most suggestive lines of approach to the problem of accounting for the current at the cathode of a mercury arc are based on considerations of space charge and of thermal equilibrium.[1] In this paper we wish to point out the significance of some recent work by Güntherschultze[2] on evaporation and conduction heat losses from a cathode and by ourselves[3] on heats of condensation of electrons and positive ions. These latter are important factors in the "energy balance" at the cathode, since the cathode is cooled by the emission of electrons from it and heated by the neutralization of positive ions at its surface.

The heat of evaporation of electrons φ_e was first measured by Wehnelt and Jenstzsch[4] and their heat of condensation by Richardson and Cooke.[5] That of positive ions has never been measured, but has been estimated from φ_e, the ionizing potential V_i and the latent heat of condensation of the neutral gas L to be[6]

$$\varphi_+ = V_i + L - \varphi_e. \tag{1}$$

This equation is obtained from the following simple cycle (Fig. 1). A positive ion at I may condense directly liberating heat φ_+. Or it may do so as at II in the following series of operations: (1) an electron evaporates from the metal, absorbing heat φ_e; (2) it and the ion recombine, liberating heat V_i; (3) the resulting neutral atom condenses in the surface liberating heat L. Comparison of the two equivalent processes leads directly to (1).

While this must be correct as regards the total heat evolved, it does not follow that all this heat must appear as heating of the electrode, since some of it may be radiated away. For instance, if the process of neutralization of the ion occurs at or just outside the surface of the electrode, half the energy is at once lost by radiation and some of the remainder is lost by reflection. Hence the actual heating of the metal φ_+ is less than given by equation (1) and may conceivably be negative. To test this matter, φ_+ was experimentally measured as follows:

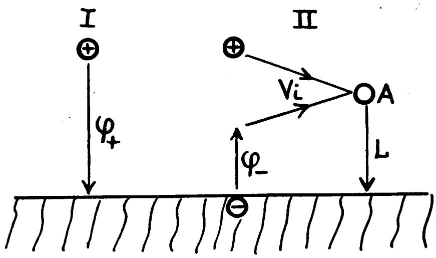

FIGURE 1

A low voltage arc in a gas (A, N_2, H_2 or Hg) was maintained between a tungsten filament cathode C and an anode A, thus creating an atmosphere of intense ionization. In this ionized gas was placed a small sphere S of the metal under investigation (Mo, Pt, etc.), which was supported by three fine leads, of which two constituted a thermojunction T to measure the temperature of the sphere and the third L served to carry the current of electrons and ions to it.

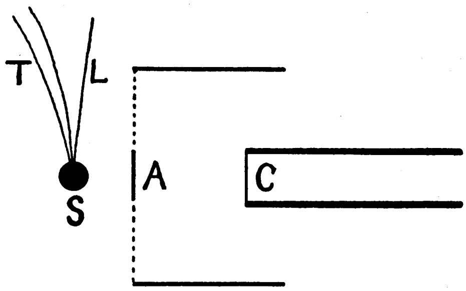

FIGURE 2

Three principal steps were involved in the experiment. First the sphere was used as a Langmuir exploring electrode[7] to determine the mean kinetic energy of agitation of the electrons and the potential of the space in its immediate neighborhood. In principle this consisted in plotting the logarithm of the electron current to the sphere as a function of its potential, which gave a curve like figure 3 in which the discontinuity D indicates the space potential V_s and the slope gives the mean energy $\bar{V}_e$ with which the electrons reach the sphere when V is less than V_s. Second, the current was set at some value, as at A, and the temperature allowed to come to equilibrium, after which the current was suddenly increased by Δi to the value B and the resulting rate of temperature rise measured. The increase of energy input which resulted from this change was

$$\frac{dH}{dt} = ms\frac{dT}{dt} = \Delta i(\overline{V}_e + \varphi_e), \tag{2}$$

where the heat capacity ms was known from the mass m and specific heat s of the sphere, the rate of temperature increase dT/dt due to current increment Δi was measured and $\overline{V}_e$ was known from the preceding measurement. Thus the heat of condensation of electrons φ_e in the metal was at once given. Third, the potential of the sphere was set at a more negative value such that the numbers of electrons and positive ions reaching it were exactly equal and the net current was zero. The temperature attained by the sphere in this condition was measured. Then that larger negative potential was found at which the sphere attained the same temperature, i.e., at which the reduction in heating due to the reduced number of electrons reaching the sphere was just compensated by the increased heating due to the increased number of positive ions and the increased field through which they fell onto the sphere. From these two voltages and the previously determined values of $\overline{V}_e$ and φ_e, together with certain minor corrections which need not be discussed here, the corresponding quantity $(\overline{V}_+ + \varphi_+)$ for positive ions was calculated. The full details of these measurements are being published elsewhere.[3] The values of φ_e thus given are extremely accurately reproducible, and yield interesting information regarding the influence of various gases and methods of surface treatment. The value of $(\overline{V}_+ + \varphi_+)$ is much less accurate, for it emerges from the calculations as the difference between two much larger quantities. Yet the value is quite definite enough to justify the following considerations.

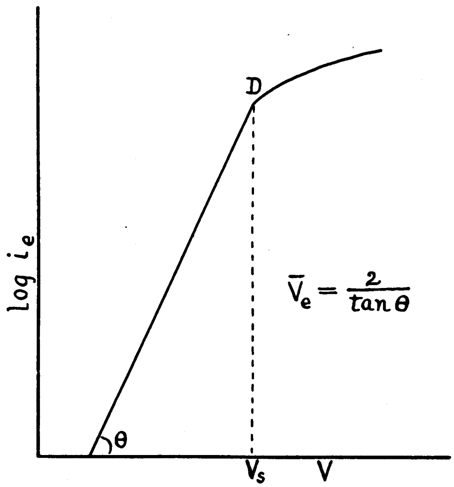

FIGURE 3

Equation (1) applied to argon ions neutralized at the surface of molybdenum leads to $\varphi_+ = 15.3 + 0 - 4.7 = 10.6$ volts, expressing all the quantities in equivalent volts. The heating effect of a positive ion is, therefore, given as more than twice that of a condensing electron. Our experiments, however, consistently gave $(\overline{V}_+ + \varphi_+)$ between 1 and 2 volts. $\overline{V}_+$ is known to be considerably smaller than $\overline{V}_e$ and hence probably less than 0.5 volt, whence φ_+ must be of the order of 1 volt. This decidedly supports the suggestion that a large portion of the energy V_i is radiated away in the process of neutralization of the ion at the surface. We should expect 50% to be radiated directly away from the metal, and perhaps 25% of the remainder to be reflected from its surface, leaving only about 5.7 out of 15.3 to represent energy of V_i actually supplied to the metal. Thus we should expect about $\varphi_+ = 5.7 + 0-4.7 = 1.0$, which is as near the experimental value as could be expected in view of our ignorance of the reflecting power of the metal under the conditions here involved, and the fact that the experimental value is uncertain within a probable range of a volt or so.

It, therefore, seems established for argon and molybdenum that equation (1) for the heating effect of a positive ion should be changed to

$$\varphi_+ = rV_i + L - \varphi_e \qquad (3)$$

in which r is less than 0.5 by an amount depending on the reflecting power of the electrode. There is every reason for extending this to other gas-metal combinations, though we are not yet ready to report on further experimental values. It is evident that φ_+ is, in general, very small compared with the value predicted by equation (1) and that it may even assume negative values.

We now turn our attention to the result of using φ_+ as given by equation (3) in place of equation (1) in calculating the energy balance at the cathode of an arc. In the cases of arcs whose electron emission from the cathode is primarily of thermionic origin (such as the carbon and tungsten arcs considered by Compton[1]) this correction makes little difference in the results, since the condensation of positive ions already contributed but a small part of the total heating. In the case of the mercury arc, however, the case is quite different. We shall base our discussion on data given by Güntherschultze[8] and corrected by Seeliger,[9] which are more accurate than the data used earlier by Compton.[1]

A. Energy lost by cathode:

		Watts per Amp. of Arc Current
(1)	By conduction from cathode spot and ultimately lost to surroundings	2.68
(2)	By evaporation of mercury from cathode (uncertainty due to lack of knowledge of temperature of escaping vapor)	2.8 to 3.9
(3)	By radiation from cathode spot	0.04
(4)	By emission of electrons, if f is the fraction of total current at the cathode which is carried by electrons	$f\varphi_e$
	TOTAL LOSS	$5.52 + f\varphi_e$ to $6.62 + f\varphi_e$

B. Energy gained by cathode:

		Watts per Amp. of Arc Current
(5)	By impact of positive ions which have fallen through cathode drop	$(1-f)V_c$
(6)	By condensation of positive ions	$(1-f)\varphi_+$
(7)	Returned from electrons	$[fV_c-(1-f)V_i]F$
	TOTAL GAIN	$(1-f)(V_c+\varphi_+) + [fV_c-(1-f)V_i]F$

In (7) fV_c is the total energy acquired by the electrons in the fall space, $(1-f)V_i$ is the energy of these electrons which is utilized in ionization, and F is the fraction of the remainder which returns to the cathode in the form of radiation, etc.

Equating A and B gives for equilibrium

$$(5.5 \text{ to } 6.6) + f\varphi_e = (1-f)(V_c + \varphi_+) + [fV_c - (1-f)V_i]F. \quad (4)$$

Substituting $\varphi_e = 3.9$ (Güntherschultze[2]), $V_i = 10.4$, $\varphi_+ = 0$ (from equation (4) with r assumed to have the same value as for molybdenum) and $V_c = 8.6$, and assuming $F = 0$, we find the fraction of current carried by electrons to be $f = 0.25$ to 0.16. If F is taken to be greater than zero, f becomes still smaller.

But it is obvious that if $V_c = 10.4$, f must exceed 0.5, for it could be as small as 0.5 only if the probability of ionization at 10.4 volts were unity so that every electron produced a positive ion. Actually V_c is almost certainly less than 10.4 and the probability is less than unity, both of which necessitate a value of $f > 0.5$ (and probably considerably greater) in order to account for the maintenance of the current. Hence our value of f calculated above is certainly far too small, which forces us to the following reconsideration of the assumptions underlying equation (4).

(*a*) The value of V_c is not known accurately. Experiments by Stark[10] gave 5.3 by the old sounding electrode method, which in the positive column gives a value about 5 volts too small.[7] Just beyond the cathode fall space the error is not so large (McCurdy[11]) so that V_c lies certainly between 5.3 and 10.3. No value between these limits, when introduced into equation (4), gives a possible value of f.

(*b*) The heat lost by evaporation in A (2) above may be over-estimated, since the mercury may escape from the cathode largely as a spray rather than as evaporating atoms. But even if this heat loss is neglected altogether, equation (4) gives only $f = 0.47$, which is still too small.

(*c*) If the electron emission is, as Langmuir[12] suggests, due to actual or partial pulling out of electrons from the cathode by the intense field due to positive ion space charge, then the cooling effect is no longer φ_e, but less. If the emission is due entirely to this process φ_e vanishes and equation (4) gives $f = 0.56$, which is a possible value, but still improbably small.

(*d*) If effects (*b*) and (*c*) coexist, f may be as large as 0.78, which is quite a reasonable value.

None of the remaining factors in equation (4) seem capable of much alteration or are able to account for the necessary value of f.

From this study we are, therefore, driven to two very important conclusions in the theory of the mercury arc: (1) Langmuir's theory that electrons are drawn out by the intense space charge field is correct. (2) The mercury lost by the cathode is in part lost in lumps or drops composed of numbers of atoms.

[1] K. T. Compton, *Phys. Rev.*, **21,** 226, 1923.
[2] Güntherschultze, *Zeits. Phys.*, **31,** 509, 1925.
[3] To be published by C. C. Van Voorhis in the *Physical Review.*
[4] Wehnelt and Jenstzsch, *Verh. D. Phys. Ges.*, **10,** 610, 1908.
[5] Richardson and Cooke, *Phil. Mag.*, **20,** 173, 1910; **21,** 404, 1911.
[6] Schottky and von Issendorf, *Zeits. Phys.*, **26,** 85, 1924; K. T. Compton, see Ref. 1.
[7] Langmuir and Mott-Smith, *G. E. Rev.*, **27,** 449, 538, 616, 762, 810, 1924.
[8] Güntherschultze, *Zeits. Phys.* **11,** 74, 1922.
[9] Seeliger, *Phys. Zeits.*, **27,** 22, 1926.
[10] Stark, *Ann. d. Phys.* **12,** 1, 1903.
[11] McCurdy, *Phil. Mag.*, **48,** 898, 1924.
[12] Langmuir, *G. E. Rev.*, **26,** 731, 1923.

SERIES SPECTRA OF SILVER-LIKE ATOMS

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The series spectra of the stripped atoms homologous with silver were investigated by Carroll[1] who identified the first members of the Principal, Diffuse and Fundamental Series of In III and the first Principal pair of Sn IV. It has now been possible to complete the identification of the first members of each of the four ordinary series for In III and Sn IV and to determine these also for Sb V.

The investigation was carried out by means of a vacuum spectrograph fully described elsewhere,[2] employing a grating of two meters radius and 30,000 lines per inch. The high-potential spark in vacuo was used as source. The standards of wave-length employed were those obtained by Mr. Smith and the author.[3] The plates obtained were of excellent definition for indium and tin especially (see Plate I); those of antimony, while not so strong, were of fair definition. Carroll's choice of the first Principal