ON THE THEORY OF THE MERCURY ARC

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Abstract

The theory of *heat balance at the cathode* is extended (1) by the introduction of the accommodation coefficient of neutralized ions, (2) by evaluation of all processes which absorb the energy gained by electrons in the cathode fall space, and (3) by correction of a previous assumption that fields sufficient to extract electrons will affect the heat of neutralization of postive ions at the surface. Test of the two resulting equations by existing experimental data shows that *Langmuir's theory* of extraction of electrons by the field at a Hg arc cathode is consistent with the cathode heat equations, but cannot be uniquely proved by them on account of uncertainty in two factors whose order of magnitude only is known: the fraction F of energy brought to the cathode by unelectrified carriers, $1.0>F>0.5$; the fraction $1/(1+\delta)$ of positive ions formed near the cathode which go to it, $1>\delta>0$.

From the net rate of evaporation an equation is obtained between vapor pressure and temperature at the cathode which, when combined with the vapor pressure-temperature equation of Hg, gives uniquely the *temperature of the cathode spot* and the *vapor pressure* outside it, provided the fraction f of total current carried by electrons is known. It is shown that the temperature of the cathode spot does not exceed 200°C, and that *the thickness of the cathode fall space is less than the electron mean free path.*

It is shown that *ionization* just beyond the cathode fall space must be of the *cumulative, multiple stage type.* From this it is shown that the fraction f must exceed 0.67 (if $\delta=0$) or 0.80 (if $\delta=1$), since these minimum values depend on 100 per cent efficiency of two stage ionization.

Mechanical pressure against the cathode by the arc is explained by the fact that the accommodation coefficient a is less than 1.0. If this accommodation coefficient of Hg ions at a liquid Hg surface should be independently measured, it would give an independent method of estimating the important fraction f.

The paper points out the causes of present limitations in our knowledge of conditions at the arc cathode and also the manner in which, and the extent to which, these limitations may be removed.

Introduction

THE early theory of Stark[1] that the current at mercury arc cathodes is of thermionic origin has been pretty thoroughly disproved by the fact that the evaporation of mercury is far too slow to justify an assumption of temperatures requisite for thermionic emission. Similarly a theory of Slepian[2] that the current at the cathode is carried by positive ions created by thermal ionization of the vapor just outside the cathode fails to suggest any physical mechanism for the input of energy into this assumed high temperature region. The theory at present in vogue is that of Langmuir,[3] who postulates "field currents" caused by the strong field which is concentrated at the

[1] Stark, Ann. d. Physik **12,** 692 (1903).
[2] Slepian, Phys. Rev. **27,** 407 (1926).
[3] Langmuir, Science **58,** 290 (1923); G. E. Rev. **26,** 735 (1923).

cathode by the processes described by Poisson's equation, and whose minimum value was calculated in the preceding paper to be at least 7.6 $(10)^4$ volts $\cdot$ cm^{-1}.

A difficulty in any theory depending primarily on electron emission from the cathode has been found in attempting to calculate from the heat balance at the cathode the fraction of the current carried by electrons, since such attempts have led consistently to values of this fraction which are too small to reconcile with the necessary amount of ionization, in view of the small cathode drop. For example, substituting direct experimental values of observable quantities in the heat balance equation has led to the conclusion that about 50 per cent of the current at the cathode is carried by electrons. Certain reasonable modifications have raised this to about 70 percent. By straining every possible factor, this proportion has been raised to about 87 percent. These values are all too small to reconcile with the fact that the cathode drop is only about 10 volts (see the preceding paper by Lamar and Compton); for 50 percent current carried by electrons would require 100 percent efficiency of ionization by them in order to obtain an equal number of positive ions to carry the remaining half of the current at the cathode. Even 87 percent would require at least 12 percent efficiency of ionization, which is still far in excess of any observed efficiencies of ionization by impact of electrons whose energy is near the minimum ionizing energy 10.4 volts.

The present paper presents some new considerations of heat balance which make it compatible with Langmuir's theory, and at the same time lead to a much more definite picture of the physical conditions in the mercury arc than has previously been possible.

It may be remarked, in passing, that the entire problem of the mercury arc is concentrated at the cathode, since the work of Langmuir and Mott-Smith,[4] Tonks and Langmuir,[5] Eckart and Compton,[6] and Killian[7] have essentially explained all other regions of a low pressure arc.

Heat Balance at Cathode

The two earliest attempts to use heat balance to investigate cathode conditions were quite unsatisfactory, the one[8] because of faulty reasoning and the other[9] because of lack of essential experimental data. Later refinements[10] have been made both in the theory and the experiments. It will be seen in the following paragraphs, however, that there are so many factors which have not previously been considered that no validity attaches to any of the conclusions thus far drawn from arguments based on heat balance.

[4] Langmuir and Mott-Smith, G. E. Rev. **27,** 449, 538, 616, 762, 810 (1924).
[5] Tonks and Langmuir, Phys. Rev. **34,** 876 (1929).
[6] Eckart and Compton, Phys. Rev. **24,** 97 (1924).
[7] Killian, Phys. Rev. **35,** 1238 (1930).
[8] Güntherschulze, Zeits. f. Physik **11,** 74 (1922).
[9] Compton, Phys. Rev. **21,** 266 (1923).
[10] Güntherschulze, Zeits. f. Physik **31,** 509 (1925); Seeliger, Phys. Zeits. **27,** 22 (1927); Elektrotech. Zeits. **49,** 853 (1927); Compton and Van Voorhis, Proc. Nat. Acad. Sci. **13,** 336 (1927); Issendorff, Phys. Zeits. **29,** 857 (1928).

We shall express the condition of thermal equilibrium by setting the total net rate of generation of heat at the cathode equal to zero, expressing each contributing item of heating or cooling in terms of watts per ampere of current. We shall let f equal the fraction of current carried at the cathode by electrons, and $(1-f)$ the fraction carried by positive ions. The processes involved in the heat balance are schematically indicated in Fig. 1 and will be discussed briefly in order.

(1) *Heating by impacting positive ions.* These ions acquire energy V_c in falling through the cathode potential drop V_c. Since the thickness of the fall space is certainly less than $1.76\ (10)^{-4}$ cm and since, as we shall see below, the ionic mean free path is considerably greater than this, we are justified in neglecting collisions of ions with vapor molecules while passing through this

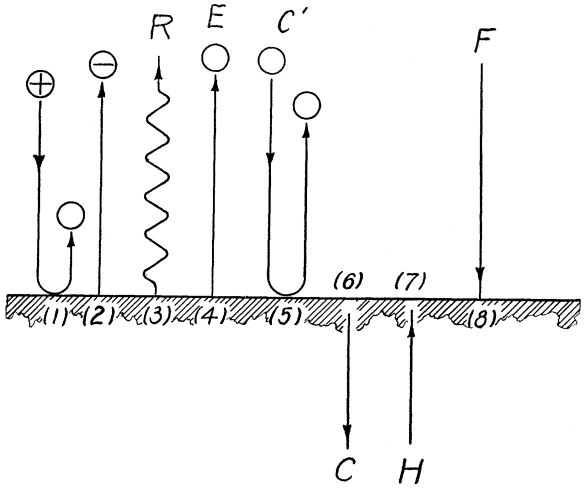

Fig. 1.

fall space. Thus the entire energy V_c is available for delivery to the cathode. To this should be added the average initial kinetic energy of the ions just before they enter the fall space. Tonks and Langmuir[4] have shown that this is negligibly small.

It is not obvious, however, that all this kinetic energy is delivered to the cathode. Let a be the fraction of it which is thus delivered, while $(1-a)$ is the average fraction which is retained by the neutralized ion after impact. This quantity a is the "accommodation coefficient" which is well known in phenomena involving the impact of gas molecules against a surface of different temperature[11] and whose existence in cases of ionic impact has been demonstrated by Van Voorhis and Compton.[12]

[11] Knudsen, Ann. d. Physik **34,** 593 (1911); **46,** 641 (1915); Langmuir, J. Am. Chem. Soc. **37,** 425 (1915); Compton and Langmuir, Rev. Mod. Phys. **2,** 184 (1930).

[12] Van Voorhis and Compton, Phys. Rev. **35,** 1438 (1930); detailed paper in preparation for physical Review.

Finally, there is the "heat of neutralization" of the positive ion, denoted by ϕ_+, whose value has been shown by an argument involving a simple cycle[13] to be $\phi_+ = V_i - \phi_- + (L)$, where V_i is the ionizing potential of the gas molecule, ϕ_- is the electron work function of the cathode surface, and L is the heat of condensation of the neutral molecule on the cathode surface. L should be used if the ion is actually condensed on the surface, but should otherwise be omitted. In our present problem L is completely taken care of in process (4) (Fig. 1).

In case the field appreciably reduces the work function (as in Langmuir's theory it reduces it to zero) it has previously been assumed that the reduced value should be used in this equation, i.e., that if the field changes the cooling effect of electron emission it will also affect the heating effect of positive ion neutralization. This is, however, not the case, as is easily shown by the following argument.

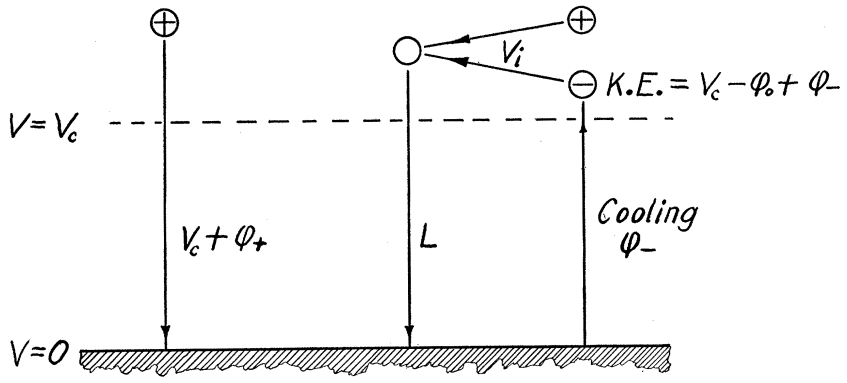

Fig. 2.

A positive ion, starting outside the cathode fall space and moving to the cathode delivers energy $V_c + \phi_+$, as indicated to the left in Fig. 2. An equivalent process is shown to the right. An electron escapes from the metal, cooling it by the amount ϕ_-. By the time it has passed through the fall space its kinetic energy is $V_c - \phi_0 + \phi_-$, where ϕ_- is the "effective" work function while ϕ_0 is the normal work function in the absence of an accelerating field. This is obvious since $(\phi_0 - \phi_-)$ is that part of the work done against the surface forces of the metal which is done by the applied field and ϕ_- is that part done at the expense of initial kinetic energy of the electron. If emission is purely thermionic, then $\phi_- = \phi_0$, whereas if emission is purely autoelectronic (as in Langmuir's theory) then $\phi_- = 0$.

Now if this electron combines with a positive ion, there is liberated additional energy V_i, and there is a further liberation of amount L when the neutralized particle condenses on the metal.

[13] Compton, Phys. Rev. **21**, 281 (1923); Schottky and Issendorff, Zeits. f. Physik **26**, 85 (1924).

Equating the net liberation of energy in the two equivalent processes gives $V_c+\phi_+=V_i+V_c-\phi_0+\phi_--\phi_-+L$, whence

$$\phi_+ = V_i - \phi_0 + L.$$

Thus the heating effect by positive ions is unaffected by the field, even though the cooling effect by escaping electrons is diminished. Physically this is easily explicable, since the cooling effect is due to the fact that only those electrons escape which, while inside the metal, possess greatest kinetic energy, a situation which has no counterpart in the process of neutralizing a positive ion.

In this equation $\phi_+=V_i-\phi_0+(L)$, it is implicitly assumed that all the energy developed by the process is retained in the cathode, which would not be the case, for example, if a fraction $(1-r)$ of it were radiated away in the process of neutralization. Compton and Van Voorhis therefore suggested[14] the modification $\phi_+=rV_i-\phi_0+(L)$, and announced experimental results indicating that $r\sim 0.5$. They later found,[12] however, that these results were due to the then unsuspected existence of an accommodation coefficient, so that there is no actual experimental measurement of r. From the fact, however, that direct measurement of the radiation from the cathode spot (process (3) Fig. 1) shows this to be almost negligible, it is evident that r is practically unity. Whatever error may be introduced in taking $r=1$ will be exactly corrected by introduction of the experimental value of heat loss by radiation in process (3).

Combining all these considerations, we have for process (1)

$$H(1) = (1 - f)(aV_c + V_i - \phi_0)$$

(2) *Cooling by electron emission.* This process of cooling is too well known to require comment, since it is well known that the electron work function ϕ_- is a latent heat of evaporation. Expressing it as a negative heating process, we have

$$H(2) = - f\phi_-$$

(3) *Cooling by radiation* is expressed directly, in terms of the observed radiated energy per ampere·sec., by $H(3)=-R$.

(4) *Cooling by evaporation* of the material of the cathode is similarly expressed by $H(4)=-E$, in which E is the product of the mass of material evaporated per ampere·sec multiplied by its latent heat of evaporation.

(5) *Cooling by gas conduction and convection* is $H(5)=-C'$.

(6) *Cooling by conduction through the cathode* is $H(6)=-C$.

(7) *Heating by an external agency*, if any, is represented by $H(7)=H$.

(8) *Heating by energy derived by electrons in the cathode fall space and indirectly returned to the cathode* can be calculated as follows. The work done on an escaping electron is V_c. If part of this work is done in pulling the electrons out of the metal (as in Langmuir's theory), this part may be expressed by

[14] Compton and Van Voorhis, Proc. Nat. Acad. Sci. **13**, 336 (1927).

$(\phi_0-\phi_-)$, where ϕ_0 is the ordinary electron work function for negligibly small accelerating fields, and ϕ_- is the actual or "effective" work function. Thus the energy with which each electron is projected out of the cathode fall space is $V_c-\phi_0+\phi_-$.

Of the total energy $f(V_c-\phi_0+\phi_-)$ thus fed into the vapor, $(1-f)V_i$ must be used to produce the $(1-f)$ positive ions which return to the cathode. We shall see below that altogether $(1+\delta)$ times this number of ions must be formed, where $0<\delta<1$, since some of the ions are formed beyond the region of potential maximum and drift toward the anode, ultimately recombining. δ is the ratio of the number of ions thus going toward the anode to the number going toward the cathode. Thus we have $(1+\delta)(1-f)V_i$ energy used in producing positive ions.

Furthermore the probe electrode measurements prove that the electrons in the negative glow near the cathode possess a considerable mean kinetic energy $\bar{V}_-$. Thus the energy fed into the vapor by electrons from the cathode, which is not expended in producing ions or retained by the electrons, is $f(V_c-\phi_0+\phi_-)-(1+\delta)(1-f)V_i-\bar{V}_-$, where the factor f does not multiply $\bar{V}_-$ since we know that in the negative glow the fraction of current carried by electrons is unity within a fraction of a percent.

Let F represent that fraction of the energy, acquired by *unelectrified* carriers from the electrons which have moved through the fall space, which returns to the cathode (as by radiation, metastable and excited atoms, high temperature neutral atoms). We have already allowed in process (1) for the energy which is brought back by positive ions, and of course none is brought back by electrons. This remaining source of heating of the cathode is therefore given by

$$H(8) = F[f(V_c - \phi_0 + \phi_-) - (1 + \delta)(1 - f)V_i - \bar{V}_-].$$

Equilibrium. Equating to zero the sum of all these eight contributions to the heating, and solving for f, we obtain

$$f = \frac{aV_c + V_i - \phi_0 - (R + E + C + C' - H) - F[(1 + \delta)V_i + \bar{V}_-]}{aV_c + V_i - \phi_0 + \phi_- - F[V_c - \phi_0 + \phi_- + (1 + \delta)V_i]} \quad (1)$$

Supplementary relation. The above expression for $H(8)$ gives us another clue to the value of f. The expression in brackets is the amount of the energy with which the electrons are shot into the vapor which is not retained by them or used in ionization. It must of necessity be greater than zero, since we know that a considerable portion of such energy is used, for example, in producing metastable or other excited atoms. In fact, we shall later discuss reasons for believing that the ionization is principally of the two stage or cumulative type. Thus from $f(V_c-\phi_0+\phi_-)>(1+\delta)(1-f)V_i+\bar{V}_-$, we find

$$f > \frac{(1 + \delta)V_i + \bar{V}_-}{V_c - \phi_0 + \phi_- + (1 + \delta)V_i}. \quad (2)$$

Values of the terms are given in Table I.

TABLE I.

Quantity	Value	Reference
V_e	10 volts	Lamar and Compton[15]
V_i	10.4	Well known
ϕ_0	4.5	Kazda[16]
R	0.04	Güntherschulze[10]
E	2.21–0	" (see below)
C	2.68	"
C'	0.0	"
H	0.0	No external heating
V_-	1.5	Lamar and Compton[15]
ϕ_-	0–4.5	(see below)
F	0.5–1.0	" "
a	1–?	" "

$E=2.21$ is based on measurements by Güntherschulze of the rate of loss of mass of the cathode, together with the latent heat of evaporation of mercury at 123°C. However, Compton and Van Voorhis suggested[14] that some of the mercury may be lost as a spray thrown out mechanically by the agitation of the surface. Such loss would not involve cooling. Issendorff[17] has verified this experimentally and has shown that the actual amount of true evaporation from the cathode spot is practically negligible as a cooling process. (Much of the spray is subsequently volatilized in the arc stream by heat developed by recombination of electrons and ions on the surfaces of the droplets, but this is not a process which cools the cathode.) It appears from this that the true value of E lies much closer to 0 than to 2.21. As to the assumed temperature of 123°C, see discussion later in the paper.

$\phi_-=0$ to 4.5, depending on the extent to which the emission is due to the field, being 0 if due entirely to the field. Perhaps a rough approximation to the right value is given by finding the effective work function which would give thermionic emission of 4000 amp·cm^{-2} at 123°C, which is $\phi_-=0.31$ volt.

F has a more restricted significance than in previous discussions owing to the more complete character of the present analysis. If the energy carried back to the cathode by unelectrified carriers is in the form of unabsorbable radiation, we should expect $F=0.5$, since the cathode subtends half the solid angle about the origin of radiation, or less than 0.5 if there is reflection at the cathode surface. Actually, however, we know such radiation to be small (see Table I). If the energy gets back by any diffusion process, as by metastable atoms or by resonance radiation, then much more than half the energy will return to the cathode since the mean free path of the diffusing particles is considerably less than the distance from the cathode to other boundaries of the vapor. Since this condition is amply fulfilled in the mercury arc, we have $1.0>F>0.5$, and it is extremely probable that F is very nearly equal to 1.0.

a has not been measured for mercury, but we should expect it to be $1.0>a>0.9$, since in other gases a approaches unity with increasing atomic weight.

[15] Lamar and Compton (preceding paper in Phys. Rev.).

[16] Kazda, Phys. Rev. **26**, 643 (1925).

[17] Issendorff, Phys. Zeits. **29**, 857 (1928).

Results for the various assumptions are given in Table II. Note first that f_2 involves the uncertain factors δ and ϕ_- and depends only on the direct application of the Energy Principle. Note also that the known fact that impact ionization processes are never very close to 100 percent efficient shows that the true value of f must be *considerably* larger than the lower limit set by f_2. The values in parentheses are impossible values either because $f_1 < f_2$, or because f_1 is negative or greater than unity.

TABLE II. $f_1 = f$ by *Eq.* (ϕ); $f_2 = f$ by Eq. (2).

			$\phi_-=0.0$			$\phi_-=0.31$			$\phi=4.5$		
		δ	1.0	0.5	0.0	1.0	0.5	0.0	1.0	0.5	0.0
		f_2	0.85	0.81	0.75	0.84	0.80	0.73	0.73	0.67	0.58
E	a	F	f_1	f_1	f_1	f_1	f_1	f_1	f_1	f_1	f_1
0.0	1.0	0.0	(0.83)	0.82	0.82	(0.81)	0.81	0.81	(0.64)	(0.64)	0.64
		0.1	(0.82)	0.82	0.83	(0.81)	0.81	0.82	(0.63)	(0.64)	0.65
		0.2	(0.82)	0.83	0.85	(0.80)	0.82	0.84	(0.61)	(0.64)	0.67
		0.5	(0.74)	0.86	0.91	(0.70)	0.84	0.89	(0.41)	(0.61)	0.71
		0.6	(−17.0)	0.90	0.95	(−0.71)	0.87	0.93	(−11.5)	(0.51)	0.74
		0.7	0.96	(1.08)	(1.02)	0.99	0.98	1.00	(4.00)	(0.49)	0.79
		0.8	0.91	(0.51)	( )	0.92	(0.55)	( )	(1.10)	(6.25)	0.90
		0.9	0.89	(0.70)	( )	0.89	(0.72)	( )	0.94	0.83	(1.21)
		1.0	0.89	(0.75)	( )	0.89	(0.75)	( )	0.89	0.75	( )
0.0	0.9	0.0	(0.82)			(0.80)			(0.63)		
		0.1	(0.81)			(0.79)			(0.61)		
		0.2	(0.80)			(0.78)			(0.58)		
		0.5	(0.59)			(0.54)			(0.26)		
		0.8	0.93			0.93			(1.08)		
		0.9	0.90			0.90			0.95		
		1.0	0.89			0.89			0.89		
2.21	1.0	0.0	(0.69)	(0.69)	(0.69)	(0.68)			(0.54)	(0.54)	(0.54)
		0.1	(0.66)	(0.67)	(0.68)	(0.64)			(0.50)	(0.52)	(0.53)
		0.2	(0.61)	(0.65)	(0.68)	(0.60)			(0.46)	(0.49)	(0.53)
		0.5	(−0.07)	(0.50)	(0.63)	(−0.06)			(−0.04)	(0.33)	(0.50)
		0.8	(1.34)	(2.70)	(0.47)	(1.35)			(1.62)	(23.0)	(0.36)
		0.9	(1.17)	(1.42)	(0.02)	(1.18)			(1.25)	(1.70)	(0.15)
		1.0	(1.09)	(1.09)	(—)	(1.09)			(1.09)	(1.09)	(−)
0.44	1.0	0.0	(0.80)			(0.79)	(0.79)	0.79	(0.62)		
		0.1	(0.79)			(0.78)	(0.79)	0.79	(0.61)		
		0.2	(0.78)			(0.76)	(0.79)	0.80	(0.58)		
		0.5	(0.58)			(0.55)	0.86	0.84	(0.32)		
		0.8	0.99			(1.01)	0.99	1.00	(1.21)		
		0.9	0.94			0.95	0.85	(1.33)	1.00		
		1.0	0.92			0.92	0.83	( )	0.92		

Conclusions. A survey of Table II shows, first of all, the futility of attempting to determine the fraction f by heat balance methods, since the unknown parameters E, a, F, leave a great range of possibilities. Nevertheless some interesting information can be obtained.

Obviously no adjustment of ϕ_-, a, F, δ will give possible results if E is as large as Güntherschulze's value 2.21, which checks the later estimates described above, which make $E << 2.21$.

It is probably hopeless to try to measure F and δ. Physical considerations, mentioned above, however, place $1.0 > F > 0.5$ (with F probably nearer 1.0 than 0.5. Similarly we shall see that $1.0 > \delta > 0$.

With these possibilities in mind, we see from Table II that the most probable values of f arise from cases where *both the numerator and denominator of Eq.* (1) *are negative,*—which means that a very appreciable role is played by the heating effect of energy which reaches the cathode by unelectrified carriers, an observation which is suggestive of a considerable concentration of

metastable atoms and of cumulative ionization. More direct evidence of this appears later in the paper.

In the light of this study it seems hopeless to prove or disprove the Langmuir theory by heat balance arguments. *This analysis shows for the first time, however, that the heat balance may be made consistent with Langmuir's theory and with the known facts of ionization* by making the most reasonable assumptions regarding the unknown factors F and δ. In order to make the considerations still more precise, it is important to measure the accommodation coefficient a for Hg ions at a Hg surface and to obtain a more reliable estimate of evaporation E under conditions in which the other thermal quantities are also measured. Thus we may assume Langmuir's theory, with its very small value of ϕ_-, on the basis of its reasonable character and the absence of evidence for any other adequate mechanism.

Temperature and Vapor Pressure at Cathode

The temperature and vapor pressure at the cathode can be calculated if the rate of evaporation from the cathode is known. Early attempts to measure this led to erratic and large values. Schaefer[18] found 36.7 $(10)^{-3}$g·amp. sec^{-1}, and Güntherschulze[10] 7.2 $(10)^{-3}$g·amp·$^{-1}$ sec^{-1}. Compton and Van Voorhis' suggestion[14] that these large values arise from mechanical spray was verified by Issendorff,[17] who found <1.3 $(10)^{-3}$ g·amp·$^{-1}$ sec^{-1}. Recently Kobel[19] devised a means for holding the cathode spot quiescent and found the rate of evaporation to be 0.017 $(10)^{-3}$ amp·$^{-1}$ sec^{-1}. Since this lies within Issendorff's limits, and since a quiescent spot would be expected not to eject spray, we shall take this as the best value at present available. (The device for holding the spot quiet may have made this value too small, but several considerations indicate that such an error is small, if present.) Kobel's average current density was 1912 amp·cm^{-2}, hence the rate of evaporation was 0.0325 gm·cm^{-2}.

It must be observed, however, that these values refer only to the *net* rate of escape of Hg atoms. The true rate of evaporation is larger than this, but a certain portion of the evaporated atoms return to the cathode as ions. The true rate of evaporation M can be equated to the observed rate M_0 plus the rate of return of ions to the cathode, which is 0.00209 $(1-f)$ g·amp·$^{-1}$ sec^{-1}. (0.00209 is the electrochemical equivalent of Hg). If we express this in terms of evaporation per cm^2, we have

$$M = M_0 + 0.00209(1 - f)j, \tag{3}$$

where j = current density. From the familiar kinetic theory relations

$$n = \tfrac{1}{4}N\bar{v}, \quad p = \tfrac{1}{3}Nm\bar{v}^2 = NkT, \quad M = nm$$

we find

$$p^2 = \frac{16}{3}\frac{M^2kT}{m} \text{ dynes} \cdot \text{cm}^{-2}, \tag{4}$$

where m is the mass of an atom in grams.

[18] Schaefer, Diss. Darmstadt (1910).

[19] Kobel, Phys. Rev. **36**, 1636 (1930).

If the experimental values of M from Eq. (3) are substituted into Eq. (4), an infinite number of pairs of possible values of pressure p and temperature T is found. Only one of these pairs of values, however, satisfies the vapor pressure relation between p and T. Thus Eq. (4) together with the vapor pressure equation, serve simultaneously to fix unique values of T and p. This value of T is the temperature of the cathode spot and from p and T we can find the value of atomic and electronic mean free paths just outside the cathode.

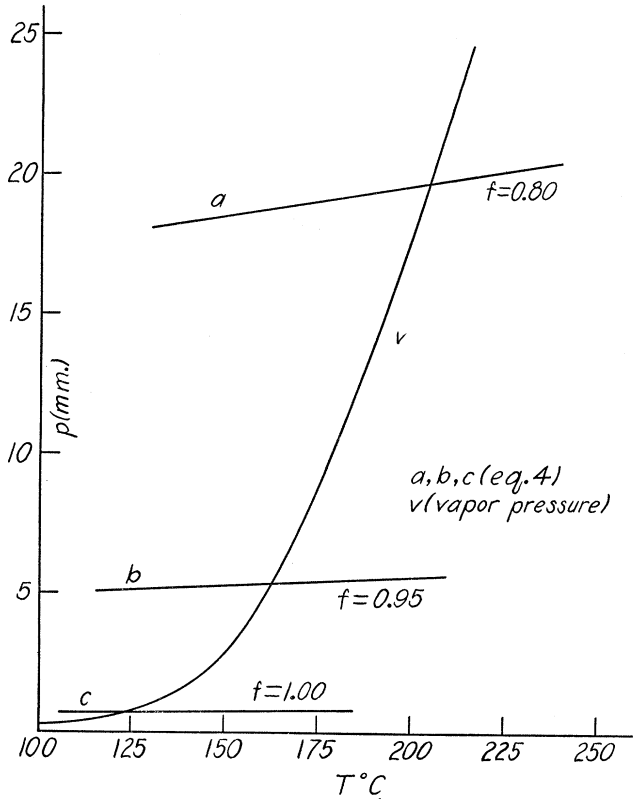

Fig. 3.

Here, as before, uncertainty in f prevents us from drawing definite conclusions, but here again we can set certain limits with considerable assurance. If ionization is cumulative in two stages, not more than one ion can be formed

TABLE III.

f	p	T	λ(electron)[20]	d_c
1.00	0.75 mm	123°C	0.0026 cm	(0.000176) cm
0.95	5.4	167	0.00033	0.000039
0.80	19.6	202	0.000084	0.000019

[20] Constants from Compton and Langmuir, Rev. Mod. Phys. **2**, 208 (1930).

for every two electrons, and if half the ions move toward the anode, recombining ($\delta=1$), we must have $f>0.8$. Table III shows the results of three assumptions, the values being taken from Fig. 3. For comparison there are shown also the corresponding values of thickness of cathode fall space, calculated as in the preceding paper.

Three important facts are derived from this consideration of rate of evaporation: (1) the surface temperature of the cathode spot cannot exceed about 200°C; (2) the vapor pressure there is considerably less than the value of about one atmosphere recently assumed;[21] (3) the electron mean free path is, in any case, considerably longer than the thickness of the cathode fall space, a fact which justifies several simplifying assumptions such as the applicability of the simple space-charge equation in the fall space.

Question of high-speed ejection of vapor. Tangberg[22] for a copper arc and Kobel[19] for a mercury arc have called attention to the relatively large pressure on the cathode spot and have interpreted it as indicating very high speeds of evaporating atoms, speeds characteristic of temperatures of the order of 500,000°K! Among the physical difficulties of this interpretation may be mentioned the inconsistency between such a temperature and the observed rate of evaporation which, as we have seen, indicates a surface temperature of not more than 200°C. Compton[23] suggested that a more reasonable interpretation of this pressure is to be found in the existence of an "accommodation coefficient" for ions which strike and are neutralized at the surface—this accommodation coefficient having been inferred for He, Ne and A ions from thermal measurements at cathodes by Van Voorhis and Compton[12] and later measured directly for He ions by Lamar.[24]

For the mercury arc, the pressure resulting from an accommodation coefficient $a<1.0$ may be calculated thus, per cm²:

Positive ion current at cathode	$j(1-f)$ amp.
Mass of positive ions striking cathode per sec.	$0.00209\,j(1-f)$ g
Number of positive ions striking per sec.	$0.63(10)^{19}\,j(1-f)$
Kinetic energy of incident ion	$1.59(10)^{-11}$ erg
Total kinetic energy of ions striking per sec.	$1.00(10)^{8}\,j(1-f)$ erg
Total kinetic energy of neutralized ions leaving cathode per sec.	$1.00(10)^{8}\,j(1-f)\,(1-a)$ erg
Total momentum of neutralized ions leaving cathode per sec.	$647\,j(1-f)\,(1-a)^{1/2}$ dyne.

This last quantity is the pressure, provided the neutralized ions leave normally to the surface. We should rather expect the escaping neutralized ions to be scattered in all directions, and in fact Lamar's results indicate this

[21] Güntherschulze, Zeits. f. Physik **11,** 74 (1922); Langmuir, Science **58,** 290 (1923); Compton, Summer Convention A.I.E.E. (1927).

[22] Tanberg, Phys. Rev. **35,** 1080 (1930).

[23] Compton, Phys. Rev. **36,** 706 (1930). (In this paper there is a numerical error which arose through taking an incorrect value for the electrochemical equivalent of Hg, but which, qualitatively, does not vitiate the argument).

[24] Lamar (to be reported at Washington Meeting of the Amer. Phys. Soc.) and published in the Physical Review.

in the case for He ions. In this case we must use the mean normal component of momentum, which gives just half the above values. We thus have

$$\begin{aligned} p &= 0.66j(1-f)(1-a_n)^{1/2}\text{g}\cdot\text{cm}^{-2} \\ p &= 0.33j(1-f)(1-a_r)^{1/2} \end{aligned} \tag{5}$$

depending on whether we assume a_n (normal escape) or a_r (random escape).

Kobel's results gave an average pressure of 5.75 cm Hg (78.2 g·cm^{-2}) on the cathode spot whose average current density was 1912 amp·cm^{-2}. Substituting these values in Eq. (5) we obtain the relations shown in Table IV.

TABLE IV.

f	0.50	0.60	0.70	0.80	0.90
a_n	0.985	0.98	0.96	0.90	0.62
a_r	0.95	0.92	0.84	0.60	(—)

Since, as we have seen, experimental evidence points to a_r rather than a_n, we see that this analysis suggests that the accommodation coefficient a for Hg ions is less than the value, nearly unity, suggested by its high atomic weight, taken in conjunction with the known values of a for He, Ne and A. This again emphasizes the desirability of making a direct measurement of a for Hg ions.

MECHANISM OF IONIZATION

The fact that the cathode drop is so constantly close to 10 volts, independently of current, vapor pressure, etc., over the entire range in which a Hg arc can be struck from a liquid Hg cathode, suggests that this value is fixed by some characteristic process in the arc mechanism. It has been quite generally assumed that this process is the ionization of the Hg atoms by electron impact, and that the significance of 10 volts is, roughly, the ionization potential 10.4 volts. There are, however, three serious and probably insuperable difficulties besetting such an interpretation, as follows.

(1) The probability of ionization by an electron of 10.4 volts energy, or even a few volts more, is so small that it is difficult thus to account for the production of the requisite number of positive ions. (2) The present more refined measurements of cathode drop point to a value *less*, rather than exceeding, 10 volts, the best estimate being 9.9 volts, which makes the assumption of direct impact ionization still more unsatisfactory. (3) *If the electrons are pulled out of the cathode by the field*, the field thus does work $\phi_0 = 4.5$ volts in pulling them out, so that *the kinetic energy gained by the escaping electron is only* $9.9-4.5=5.4$ *volts, which is far insufficient to permit ionization by single impact.*

The obvious escape from these difficulties is to adopt the theory that *ionization is caused in two stages*, which is at once seen to be in excellent accord with various related facts. The electron energy is very close to the value necessary to produce excited or metastable atoms, and to ionize them when formed. We know that, unlike ionization by single impact, these processes have a high probability when the energy of the impacting electron is only

slightly in excess of the minimum energy required for the process. Furthermore, experiments with low voltage arcs have proved that the favorable conditions for arcs to operate by such cumulative ionization are large current density and vapor pressure of at least the order of 1 mm, both of which conditions are amply fulfilled in the mercury arc. *Thus it would be very surprising if the ionization were not of the cumulative type.* The reason for not having adopted this interpretation sooner was principally the difficulty, in preceding analyses of the situation, of justifiying a value of f large enough to be consistent with it, and secondarily the erroneous apparent significance of a cathode drop so nearly equal to the ionizing potential.

Electrical Conditions Near Cathode

In Fig. 4, let the ordinates of curve N represent the relative numbers of electrons, projected out from the cathode, whose free paths terminate by

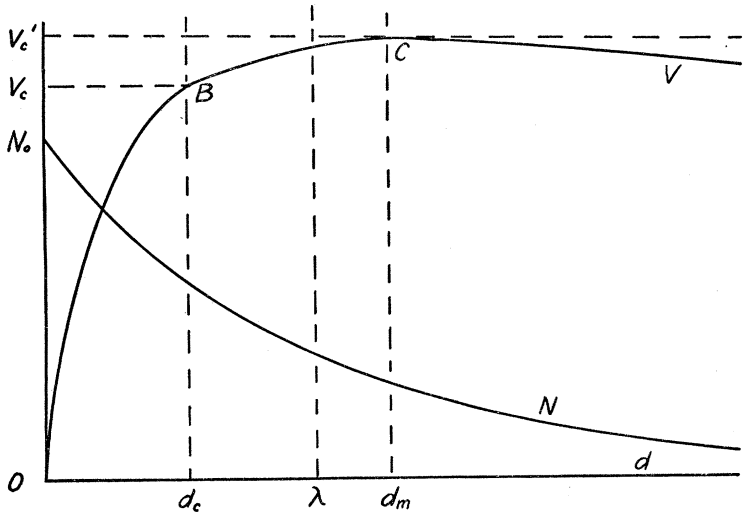

Fig. 4.

collisions at distances d. Since, as we have seen, the thickness of the fall space d_c is less than the mean free path λ, we may consider these as projected out with uniform velocities corresponding to the kinetic energy $V_c-\phi_0$. The rate of production of ions or excited atoms will therefore also be proportional to the ordinate of curve N at each distance from the cathode.

Every region of intense ionization tends to be a region of potential maximum, owing to the fact that electrons diffuse away from it more rapidly than do positive ions. There is therefore, a little way in front of the cathode, a region of potential maximum C. As a first approximation, this may be taken as being at the distance of one mean free path from the cathode, since this is the mean position at which ionization occurs.

From this region of potential maximum C, positive ions are forced by the field *in both directions*, half moving in to the cathode and half moving out

toward the anode and eventually combining with electrons. Since the cathode is so much nearer than the anode to this region of potential maximum, the concentration gradient on the cathode side must be greater than that of the anode side, which would tend to displace the region of potential maximum away from the cathode. On the other hand, the fact that ionization occurs at a more rapid rate nearer the cathode, as shown by curve N, tends partially to offset this displacement. The extent of this displacement determines the amount by which δ in Eqs. (1, 2) differs from 1.0.

The net result of these actions, including the action of space charge within the space-charge sheath (cathode fall space) is shown diagrammatically by curve V. The space charge equation applies within the distance d_c, to the point B. Between B and the potential maximum, the plasma considerations developed by Tonks and Langmuir[25] apply. Beyond C there is ambipolar diffusion toward the anode by both electrons and ions.

There is obviously a small uncertainty in the meaning of "cathode drop". The drop across the space-charge sheath to the point B is the quantity which is significant in estimating the field at the cathode. The drop to the point C is the maximum potential drop available to produce ionization. The drop to some point beyond C—i.e., to the point of nearest approach of an exploring electrode, is the nearest point to which the drop can be measured experimentally, as in the preceding paper.

In conclusion, it may be noted that this analysis indicates that the limits of uncertainty in the values of f, d_c and field at cathode may be reduced by more careful measurements of thermal relationships and of accommodation coefficient, but that the accuracy of an absolute evaluation of these quantities is limited principally by our inability accurately to measure or estimate two factors: the fraction F of the energy, imparted by electrons to unelectrified carriers, which goes to the cathode; and the fraction $1/(1+\delta)$ of the positive ions formed near the cathode which go to the cathode.

[25] Tonks and Langmuir, Phys. Rev. **34,** 876 (1929).