HEATS OF CONDENSATION OF ELECTRONS ON SEVERAL METALS IN SEVERAL IONIZED GASES

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Abstract

Heats of condensation ϕ_- of electrons on electrodes of Mo, Pt and W coated with K were measured in the ionized gases A, Ne, He, N_2 and H_2, by measuring the heat developed in Langmuir collectors of these metals when a known number of electrons of known energy were received by it. The values of ϕ_- varied as expected for the different metals, but also showed decided dependance on the surrounding ionized gas, even though this were a highly purified inert gas. The highest and lowest values recorded were 5.21 volts for Pt in N_2 and 0.93 for W+K in He. There is evidence that the specific effect of a purified gas is due to its ions rather than its neutral atoms. The accuracy of the experimental determinations is well within 1 percent.

IN A previous paper[1] a method for measuring the heat of condensation ϕ_- of electrons upon a metal collector in a gas discharge was described in detail. This method makes use of a small spherical Langmuir collector in which is imbedded a thermocouple. From the electron currents and the rates of heating at two different potentials (both somewhat negative to the space potential) and the application of some minor corrections, ϕ_- is obtained. Continuing with the same type of apparatus, additional measurements have been made on collectors of several metals in several gases. The inert gases used were all purified in the vacuum system by "misch metal" arcs, and the other gases were prepared and purified as previously described.

Corrections for the effect of contact potential difference between the collector and anode, hereafter called C.P.D., (corrections not applied in the previous paper) were found to be very necessary in order to get consistent results under some of the experimental conditions. This was due to variations in the C.P.D. following cleansing of the surface of the collector by positive ion bombardment, and was particularly evident when measurements were being made with a Pt collector. After the collector had been bombarded with positive ions accelerated by a field of a few hundred volts in order thoroughly to clean the surface and remove adsorbed gas layers, it was noticed that the electron current to the collector gradually increased while the potential of the collector, which was slightly negative to the space, was kept at the same value with respect to the anode, the general arc conditions remaining the same. The change in collector potential necessary to reduce the collector current to the value it had immediately after bombardment, is the change in C.P.D. Table I gives a typical set of results for platinum in argon extending over a period of about 1 hour after bombardment.

[1] K. T. Compton and C. C. Van Voorhis, Proc. Nat. Acad. Sci. **13**, 336 (1927); C. C. Van Voorhis, Phys. Rev. **39**, 318 (1927).

TABLE I. *Effect of contact potential difference change.*

Calculated from observations	Change in C.P.D.	ϕ_- Calculated for freshly bombarded collector
4.85 volts	0.05 volts	4.90 volts
4.78	.14	4.92
4.68	.22	4.90
4.65	.26	4.91
4.65	.27	4.92

When the previous paper was published there was considerable uncertainty as to the specific heat of molybdenum, the material of which the spherical collector had been made. Since then measurements of the specific heat of Mo have been made in two independent investigations[2,3] the results agreeing within 1 percent in the range of temperature concerned in our measurements of ϕ_-. The present paper includes the revised results obtained by using these new specific heat values, as well as the results of some new measurements of ϕ_- for Mo in He, Ne and two gases previously used, A and N. The repeated measurements were made to take account of whatever C.P.D. change there might be. However, as will be seen from the result given in Table II, this effect was negligible in the measurements previously made in A and was small in N.

The results of these measurements are assembled in Table II.

TABLE II. *Values of ϕ_- and C.P.D. changes, Δ, in volts. Δ is the change in C.P.D. measured from the instant at which the positive ion bombardment (for cleansing the surface) was stopped.*

Collector Material	Argon ϕ_-	Argon Δ	Neon ϕ_-	Neon Δ	Helium ϕ_-	Helium Δ	Nitrogen ϕ_-	Nitrogen Δ	H_2+inert gas ϕ_-	H_2+inert gas Δ
Mo	4.14	0–0.2	3.69	0–0.1	3.53	0–0.1	4.47	0–0.1	—	—
Mo*	4.12	?	—	—	—	—	4.39	?	3.79	?
							(4.19)‡	?	(3.47)	?
Pt	4.89	0–0.5	4.61	0–0.3	4.39	0–0.2	5.21	0–0.4	3.9±0.6	-
W+K†	1.11	0	1.05	0	0.93	0	—	—	—	—

* Old results[1] corrected by use of better specific heat values,[2,3] but not for C.P.D. changes, which were not measured.

† W+K was a tungsten collector coated by distillation with potassium.

‡ ( ) are doubtful, being perhaps due to a spurious C.P.D. change caused by some impurity. These lower values were not found with the new tube.

GENERAL DISCUSSION OF RESULTS

Results in the inert gases. When the previous paper[1] was published, we believed that the value of ϕ_- of a metal obtained in an inert gas discharge by this method would be the same as ϕ_- obtained by thermionic methods in a high vacuum, after correcting for the large difference in the temperatures involved in the two methods. The results show, however, that in gas discharges even in the inert gases the value of ϕ_- for a given metal depends upon the gas, for the values in A, Ne and He, respectively, differ from each other by amounts much larger than the experimental errors involved. We believe

[2] J. E. Stern, Phys. Rev. **32**, 298 (1928).

[3] D. Cooper and G. O. Langstroth, Phys. Rev. **33**, 243 (1929).

that these differences are not due to differences in the amounts of active impurities in the respective inert gases, because the values of ϕ_- appear to be perfectly definite and reproducible, once the gas and apparatus are well cleansed, and are not modified by further strenuous purification.

Because of the following results obtained in mixtures of inert gases we suggest that these differences in the values of ϕ_- may be due to a layer of gas atoms or positive ions, probably the latter, on the collector. With a Pt collector in a 50%−50% Ne−A mixture, ϕ_- was 4.92 and 4.78 volts in 16 and 22 volt arcs respectively. In a 75%−25% He−A mixture ϕ_- was 4.80 and 4.68 volts in 18 and 30 volt arcs respectively and in a 50%−50% He-A mixture ϕ_- was 4.91 and 4.77 volts in 18 and 30 volts arcs respectively. Thus with an arc voltage lower than the ionizing potential of one of the gases in the mixture, the value of ϕ_- is near that characteristic of the gas with the lower ionizing potential, but with an arc of voltage high enough to ionize both gases, the value of ϕ_- is between the values of the two pure gases.

Also after the collector was bombarded with 200–300 volt positive ions in an inert gas mixture the C.P.D. *increased* for a short time immediately after bombardment when the arc voltage was high enough to ionize both gases, but when the arc voltage was high enough to ionize only one gas the C.P.D. decreased immediately after bombardment. This effect was rather small but was found in 50%–50% mixtures of any two of the inert gases used. Thus in the A−He mixture with a 30 volt arc the C.P.D. increased about 0.02 volt to a maximum in about 15 seconds, then decreased about 0.06 volt in the next minute; but with an 18 volt arc there was only the decrease of 0.06 volt starting immediately after bombardment. In the A-Ne mixture with a 25 volt arc the increase in C.P.D. was 0.015 in the first 30 seconds and then a decrease of 0.06 volt in the next two minutes, while with a 17 volt arc there was only the 0.06 volt decrease in C.P.D. during about 150 seconds after bombardment. In the He-Ne mixture with a 30 volt arc there was an increase in C.P.D. of 0.05 volt in 30 seconds and then a decrease of 0.09 volts in the next two minutes, whereas with a 21 volt arc there was only a decrease of about 0.06 volt in about 35 seconds starting immediately after bombardment.

These results, indicating that the specific influence of the inert gas on ϕ_- is due to its ions rather than to its atoms, further suggest that it arises from the halogen-like character and hence great chemical activity of the ions, which may lead to a prolonged period of attachment of the ion to the metal during the process of its neutralization. If each incoming positive ion were to remain in contact with the surface for 0.001 second the surface would be about 10 percent covered with ions.

General discussion. The new results for ϕ_- with a Mo collector in argon (see Table II) agree well with the corrected results from the former measurements while in nitrogen the new ϕ_- value differs from the old higher value by about the amount of C.P.D. corrections, but with the new tube there did not seem to be enough evidence of a lower value also, to warrant its inclusion in the table. The values of ϕ_- with a Pt collector have been calculated with

the use of the specific heat equation $C_T = 0.03165 + 0.0000060t$, based on the results of Magnus[4] and White,[5] and show the same order of variation as with Mo in the inert gases and nitrogen, but the values of ϕ_- with hydrogen present in the discharge were quite variable and not at all reproducible. It was not possible to maintain the discharge in pure hydrogen and though the hydrogen content of the gas mixtures was "cleaned up" rather rapidly, this is not the whole cause of the variableness of the results as the changes were not progressive but more or less random.

Similar variableness in results was found in the measurements of ϕ_- with a tungsten collector in argon, the values obtained ranging from 2.0 to 3.2 volts, in spite of prolonged attempts to get steady conditions. The fact that the tungsten used was ordinary thoriated "C" grade used in the lamp industry may account for these low values and the variableness of these results, but, because of this uncertainty, the values are not recorded in Table II. After a small amount of potassium had been vaporized into the discharge tube in the neighborhood of the W collector, the results were quite steady and reproducible, giving the values recorded in Table II. The specific heat equation used in calculating the W results was $C_T = 0.03194 + 0.00000613t$ from Zwikker[6] which is in good agreement also with the more recent results of Magnus and Holzmann.[7] With the potassium in the discharge tube no C.P.D. change was observed.

Accuracy of the results. The mean values given in Table II are the means of from 10 to 50 separate determinations of ϕ_- none of which differed from the mean by more than 0.10 volts, the rare values having a larger variation being discarded. Also each mean value is the result of averaging the results from at least three fillings of the gas used, in many cases other fillings of other gases being interspersed. In many cases under good experimental conditions the maximum variation in a series of 6 to 8 results would be less than 0.05 volts.

A small correction[8] to take account of reflected electrons probably should be made. Any such correction should be *subtracted* from the values given for ϕ_- since the reflected electrons have delivered some of their energy to the collector. Just how large this correction should be is rather difficult to estimate since the average incident energy of the electrons is of the order of one volt and the measurements of Petry[9] and others have shown that the reflection coefficient of slow electrons varies greatly with the surface conditions of the collector. However, since the reflection coefficient is small for slow electrons striking a collector covered by a gas layer we believe this correction to be less than 0.10 volt. In any case such a correction is too small and in the wrong direction to account for the difference in ϕ_- in the different inert gases.

[4] A. Magnus, Ann. d. Physik **48**, 997 (1915).

[5] W. P. White, Phys. Rev. **12**, 436 (1918).

[6] C. Zwikker, Zeits. f. Physik **52**, 668 (1928).

[7] A. Magnus and H. Holzmann, Ann. d. Physik **3**, 598 (1929).

[8] The need for such a correction was called to our attention by H. M. Mott-Smith after the publication of the previous paper.[1]

[9] R. L. Petry, Phys. Rev. **26**, 346 (1925) and Phys. Rev. **28**, 362 (1926).

Conclusion

Our results show conclusively that ϕ_- in a gas discharge depends not only upon the material of the collector or cathode but also upon the gases in which the discharge takes place even though very pure inert gases are being used. Even a very slight impurity in the gas or collector material may lower the value of ϕ_- by a large amount. Consequently in evaluating the energy balance at the electrodes, fairly large errors may be made unless the value of ϕ_- for the existing experimental conditions is determined and used in the calculations.

In conclusion we wish to express our thanks to Mr. Donald C. Archibald who helped with the experimental work upon which this paper is based.