THE CRITICAL POTENTIALS OF METALLIC VAPORS: I. COPPER

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Abstract

Using a method for determining the critical potentials of metallic vapors in which the metallic vapor is produced in the neighborhood of a gauze by vaporization of the gauze, it has been found possible to determine a number of critical potentials in Cu vapor in the region 0–20 volts. The values found in the region 0–11 volts, can be identified from the spectroscopically known energy levels. The interpretation of those above 11 volts is incomplete. Some of them agree with soft x-ray levels found by Thomas, and some with second ionization potentials determined by Russell. Whether the remaining levels correspond to spark terms or not remains to be seen.

Introduction

SINCE the amount of work being done on the organization and interpretation of the spectra of the metals has increased recently, a determination of the critical potentials of these elements becomes important as a check on the energy states of the atoms and the series limits of the spectra. Incidentally, such a determination will also serve as a check on recent theory of spectra.

Unfortunately the method of Franck and Hertz[1] and its modifications which yield such definite results in the case of those elements that can exist in the gaseous state at low temperatures cannot be used for those elements that require a high temperature for the production of the necessary vapor density. In the case of copper, for instance, a temperature of about 1300°C is required to produce a vapor pressure of 10^{-3} mm and at those temperatures insulation difficulties are such as to discourage experimentation.

It was in order to find a method which would remove some of these difficulties that the present work was undertaken. Obviously, if the metallic vapor and the heated portions of the tube containing the electrodes can be localized so that the leads to the outside can be kept cool and free from the deposits of metal, no difficulty with insulation should be experienced.

Experimental Arrangement

A modification of the three-electrode method was finally adopted. The chief difference lies in the fact that whereas in the method originally used the gas filled the whole tube, in the present scheme the gauze to which the electrons are accelerated is made of the metal under investigation, and this is heated by an electric current to such a temperature that vaporzation takes place. The maximum vapor density will then be in the neighborhood of the gauze, and the rest of the tube will be comparatively free from

[1] For a discussion of the methods used hitherto see Franck and Jordan's "Anregung von Quantensprüngen durch Stösse, Berlin (1926).

vapor. Electrons accelerated from the source to the gauze will at most make only a few impacts with atoms of the vapor before reaching the neighborhood of the gauze, and the energy loss due to momentum transfer will be slight. Thus the doubtful objection to critical potential determinations raised by some writers, viz., that the electrons do not reach the gauze with their full energy, is removed.

Fig. 1 shows the arrangement of electrodes used. S is an oxide-coated platinum plate which served as an equipotential source of electrons. This was heated from behind by the radiation from a flat tungsten spiral. D_1 is a diaphragm with a hole 5 mm in diameter, G is the gauze, D_2 is a second diaphragm, and R is the receiving electrode. These were enclosed in a Pyrex tube which was evacuated to a pressure between 10^{-5} and 10^{-6} mm. The gauze was heated by a direct current to the desired temperature. In order to keep the potential drop across the gauze as low as possible and thus prevent a change in the velocity distribution of the electron stream due to this drop, it was found advisable to work with gauzes of low resistance, and as a consequence, to use large currents for heating. In this work the potential drop across the gauze was about 0.5 volts and the drop across that portion directly opposite the hole in the diaphragm D_1 about 0.1 volt. The middle point of the gauze was connected to D_1, as shown in the diagram. The two were thus effectively at the same potential.

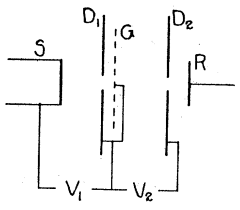

Fig. 1. Arrangement of electrodes.

The gauze was made by drilling holes in a piece of sheet copper 0.025-0.03 mm thick. With this thickness, a current of 15-20 amperes was sufficient to give a temperature of about 1050° which was found sufficient to produce the necessary vapor density. The temperature of the gauze was not uniform and portions of it may have been at a higher temperature.

Because of the magnetic field set up about the gauze, electrons accelerated from the source would not pass directly to the receiving plate, but would be deflected. It was necessary therefore to have the diaphragm D_2 slotted with the long axis of the slot perpendicular to the magnetic field.

A variable accelerating potential V_1 was applied between the source and D_1 and a constant accelerating potential of 2 volts between D_1 and D_2. A potential was also applied between D_2 and R to reduce the secondary emission from the receiving electrode. A shunted quadrant electrometer was used to measure the current. For currents such that a shunt resistance of 10^7 ohms or less was sufficiently high, "Glastor" grid leaks were found to be remarkably steady. When higher resistances were required, graphite marks on hard rubber were used.

The current was measured for various values of V_1 keeping V_2 fixed and the current-voltage curve plotted. The current was measured at 0.2 volt intervals between 1 and 20 volts.

Fig. 2 shows the types of curves obtained in the region 2-8 volts. Fig. 3 gives a magnified portion of another curve in the region 0-4 volts. Plotted to this scale, the breaks become somewhat more prominent. While the breaks are far from ideally sharp, they can still be determined with a good degree of accuracy when, as was the case here, the current is measured at equal voltage intervals. Then a change in slope corresponding to a break becomes noticeable through an increase in the difference between successive values of the current. The critical voltages can then be determined from the data directly, instead of from the curves. Since the current was measured at 0.2 volt intervals, the breaks could be accurately located within this range of voltage on any given curve.

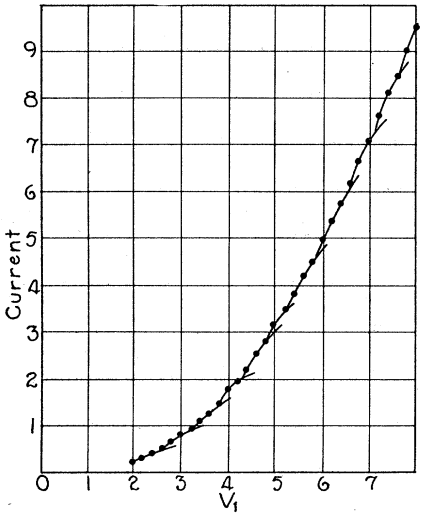

Fig. 2. Critical potential curve in the region 2 to 8 volts.

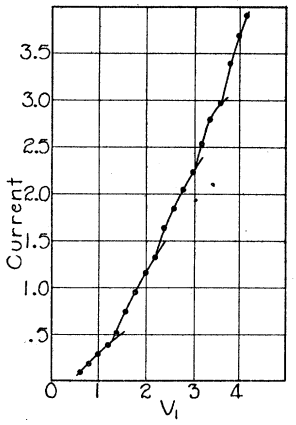

Fig. 3. Magnified portion of another curve.

In determining the critical potentials one break was taken as standard and assumed to be known, and the others determined in terms of this. This is equivalent to correcting for the contact e.m.f. between the oxide coated electron source and the gauze. This correction varied with the condition of the source, but in most cases was not more than 0.3 volt. The surprisingly low value of this correction may be due to metallic vapors depositing on the oxide plate and thus changing its nature.

Discussion of Method

In order to understand the shape of the critical potential curves, it will be well to consider the type of curve which might be expected under ideal conditions. Suppose that all the electrons emitted from the source had exactly the same velocity. With no vapor present a curve similar in shape to a current-voltage thermionic curve might be expected. If vapor were present

around the gauze but if no inelastic impacts occurred, some of the electrons would be scattered by impact with atoms of the vapor and would not pass through the opening in D_2. The result would thus be a general lowering of the curve. If, however, at a critical voltage, some of the electrons would make inelastic collisions with atoms of the vapor, these would, under the action of V_2, move toward the opening in D_2 and would become noticeable through an increase in the current to the receiving electrode. The effect would thus be a decrease in the scattered current due to the energy loss of some of the electrons. As the accelerating potential is increased, the electrons which suffer critical energy losses would retain some of their energy after impact, would again be scattered, and the current would decrease.

If instead of an isolated energy level, a gap, bounded on both sides by energy levels so close together that they could not be resolved by this method, were present in the energy level diagram, one would expect a decrease in the current as the energy of the electrons from the source exceeds the energy necessary to remove an electron from the lowest level of the atom to the level forming the lower boundary of the gap. When the voltage corresponding to the upper level is reached, there would again be an increase in the current.

Since the energy levels just below the level corresponding to ionization lie close together, it is to be expected that at the ionization potential an increase in the electron current without the preceding decrease would take place. This increase would be due chiefly to the electrons removed from the atoms.

These ideal conditions could not be approximated in the present experiments. The actual velocity distribution was such that the greater portion of the electrons had velocities extending over a range of about 1 volt. The effect of this would be, first, to make the breaks less sharp; and, secondly, to remove the decrease in the current following a critical potential. A reference to Figs. 2 and 3 shows that the experimental curves bear out these conclusions.

Three other factors besides inelastic collisions might enter into these experiments to influence the appearance and position of these breaks. First, it is well known in critical potential work that any change in the space charge around the gauze, such as would take place when the electrons lose their energy, will change the direction and magnitude of the electron stream; and, secondly, a selective scattering without loss of energy at a critical potential such as was first observed by Maxwell[2] and by Dymond[3] might produce an effect. The vapor available in most of the runs was so low that any change in space charge would probably not be noticeable. However, in order to determine definitely if these two factors have any influence, curves were taken with V_2 reversed and equal to 2 volts so as to retard the electrons. It was found that the breaks completely disappeared.

[2] L. R. Maxwell, Proc. Nat. Acad. Sci. **12**, 509 (1926).
[3] E. G. Dymond, Phys. Rev., **29**, 433 (1927).

This would not be the case if they were due to space charge or to selective scattering without energy loss.

The third factor which might play an important part is the emission of secondary electrons from the gauze or receiving electrode when bombarded by the primary beam. Farnsworth,[4] Petry,[5] and others have shown that there are definite critical changes in the magnitude of the secondary electron current from solids, when the velocity of the primary beam is changed. Any breaks which originate from these secondary electrons should persist if the gauze temperature were lowered. It was found that, if the temperature of the gauze was lowered so that no appreciable vaporization took place, the breaks completely disappeared.

It may be of interest to mention that if the critical potential curves were taken soon after the gauze had been introduced into the tube and before outgassing had progressed very far, that the breaks could be observed at a lower gauze temperature than when the outgassing was more nearly complete. An increased vaporization during outgassing, such as was first observed by Berliner,[6] would account for this. In addition to this increase in the vapor density, the increased gas pressure in the tube during outgassing would retard the diffusion of the vapor away from the gauze and would therefore act to increase the vapor density in the neighborhood of the gauze. Both these factors would increase the probability of the electrons making inelastic collisions and would enter into the explanation of the observed fact.

Discussion of Results

The spectrum of copper has been investigated by Shenstone,[7] Sommer,[8] and by Russell[9] and his co-workers. As will be seen from a comparison of the critical potentials calculated spectroscopically with the values obtained from these experiments (Table I), the agreement is quite close. The values given here differ slightly from those published in a preliminary notice which appeared in Nature,[10] but the difference is within the limits of experimental error.

These values are the average of from six to ten determinations. In no case is the maximum variation from the mean more than 0.2 volt, and in most cases less than that. The values enclosed in brackets are uncertain, because of possible overlapping of the error in the determination. Those marked "questionable" could only be repeated intermittently. A series of values were obtained between 2.1 and 2.6 volts which probably correspond to a group of critical potentials lying in this region. The variation was a

[4] H. E. Farnsworth, Phys. Rev. **20**,p. 358 (1922).
[5] R. L. Petry, Phys. Rev. **26**, 346 (1925).
[6] A. Berliner, Ann. der Physik **33**, 289(1888).
[7] A. G. Shenstone, Phil. Mag. **49**, 951 (1925).
[8] L. A. Sommer, Zeits. f. Physik **39**, 711 (1926).
[9] H. N. Russell, Astrophys. J. **64**, 184 and 233 (1927).
[10] H. B. Wahlin, Nature, p. 585, Oct. 22, 1927.

TABLE I. *Critical potentials in Cu and their interpretation.*

Critical potentials (volts)	Spectroscopic values	Transitions (Sommer)	Thomas' soft x-ray values	Russell's values (from spark)	Comment
1.38	1.38	$1^2S-{}^2D_3$			
2.0–2.6	2.13–2.39	${}^2D_{2,3}-2^2P_{1,2}$			
3.18	3.18	${}^2D_2-{}^4P_3$			questionable
3.73	3.77	$1^2S-2^2P_1$			
4.2	4.46	${}^2D_2-3^2P_1$			
4.8	4.87	$1^2S-{}^4P_3$			
5.67	5.75	$1^2S-{}^2D_3$			
6.09	6.09	$1^2S-3^2P_2$			
6.61	{6.65} {6.52}	${}^2D_2-{}^2D_3{}^2$ 1^2S-3^2S			
7.06	7.10	${}^2D_2-{}^2G_5$			
7.72	7.69	$1^2S-\infty$			
8.14	8.28	$1^2S-{}^2D_3$			
{8.71} {9.0}	8.73	$1^2S-{}^2G_5$			
	8.95	${}^2D_2-\infty$			
9.42	9.27	$1^2S-{}^2P_1$			
9.98	10.01				
10.85	10.90	$1^2S-\infty$			
11.63					
12.4			12.3		questionable
13.06					
14.0			14.2		
14.92					
15.52			15.7		
16.6					
17.16				17.1	
17.60				17.6	questionable
18.12					
{18.60} {19.00}			19.0		
19.68					

little too great to be ascribed to an experimental error in the determination of a single transition. These, together with the 3.18, 4.2, and the 7.06 values, are of interest since they could not be explained as due to transitions from the normal state of the atom. They agree reasonably well with transitions from the metastable ${}^2D$ state which serves as the ground level of the doublet-quartet series. In oder to have atoms in this state they would either have to be brought there by electron impact or else be vaporized in this state. A measurable positive ion current from the gauze was obtained even with $V_1=0$. If some of the Cu atoms come off positively charged, one might reasonably expect some of the atoms to be vaporized in the metastable ${}^2D$ state also. The number that would be produced in this way would probably be too small to be detectable. A study of these positive ion currents is being undertaken.

The alternative explanation of these transitions from the metastable state is that the atoms are brought into this state by electron impact. This means that in order to have transitions from this state, the atoms must have been struck twice by electrons. If this is the case, a decrease in the electron current should cause the breaks to disappear, since the probability of the transition would vary as the square of the current. It was necessary

to run the oxide source at a high temperature to prevent, as much as possible, the condensation of metallic vapors on it and thus changing the space current so that it was impossible to vary the current sufficiently to test this point with the present arrangement. It is hoped that further experiments will settle this question.

The critical potential at 9.42 volts may correspond to an ionization potential (the spectroscopic value given by Russell is 9.5 volts). The ionization potential at 10.85 volts agrees better with Russell's value (10.87 volts) than with Sommer's (10.90 volts), but the difference between these values is so small that it is impossible to determine from these experiments which is more nearly correct.

Our knowledge of higher critical potentials is still too scant to draw any definite conclusions about the values above 10.85 volts. The soft x-ray levels found by Thomas, together with the second ionization potentials given by Russell, have been listed for comparison. With a further knowledge of the spark term, it may be possible to determine to what the undesignated ones correspond.

While the method described above is far from ideal in that the breaks do not appear sharp on the curves, it has one important advantage over the three-electrode method as applied in earlier critical potential work, particularly in gases. In this work, V_2 was applied so as to retard the electrons coming through the gauze. Those electrons that made inelastic collisions were thus kept from reaching the receiving electrode. The effect on the current-V_1 curve was that at a critical potential there was a decrease in the current and a "hump" appeared in the curve. There has always been a question as to what points on successive humps should be taken for comparison. In the present method this difficulty does not enter, since the sharp increase in the current appears at the voltage where the inelastic collisions begin.

It is difficult to say just what range of metals can be covered by the present method. It seems likely, however, that for those metals that require a temperature of more than 1200 or 1300°C for the production of the necessary vapor density, radical changes will have to be made. At this temperature, thermionic emission from the gauze will become appreciable and may create a space charge around the gauze so as to alter the results.

A rather surprising thing is that the breaks appear as sharp as they do at the vapor densities available. The vapor pressure of copper at the melting point, and that was, of course, the limiting temperature that could be used in these experiments, is of the order of 10^{-4} mm, when the copper is thoroughly outgassed. At this pressure, the critical potentials should barely be noticeable. However, the good agreement of the values found with the ones calculated from spectroscopic data, together with the other evidence given earlier in this paper, leads to the conclusion that they originated in the vapor. The work is being extended to other metals.

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