IONIZATION AND RESONANCE POTENTIALS IN GALLIUM AND INDIUM

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ABSTRACT

The critical potentials of gallium and indium have been experimentally determined by the method of inelastic impact. A simple three-electrode tube and the Hertz-differential tube as a simple three-electrode tube or as a four-electrode tube were used. Ionization was detected by the modified space charge method, by the Lenard method, and by the change in the gap resistance. The following critical potentials below ionization were observed: in gallium vapor 3.07 v. $(2p_2-2s)$, 4.22 v. $(2p_2-3d_2)$, 2.70 v. $(2p_1-2s)$, 3.8 v. $(2p_1-3d)$; in indium vapor 0.30 v. $(2p_2-2p_1)$, 3.03 v. $(2p_2-2s)$, 4.07 v. $(2p_2-3d_2)$, 2.8 v. $(2p_1-2s)$. Two ionization potentials were observed: in gallium vapor 5.8 and 13.2 v.; in indium vapor 6.3 and 14.1 v. The ionization potentials are judged to be accurate to 0.5 volts.

INTRODUCTION

THE importance of the exchange of energy between a colliding electron and atom or molecule and the relation of the energy exchanged in spectral excitation is well recognized. The results obtained by the method of electronic excitation have been analyzed with success on the basis of the quantum theory. Thus critical potentials are extremely valuable in establishing the orbital levels of the valence electron. The validity of the theory is further established by the step-wise excitation of lines or groups of lines of the arc series. The excitation of the single line 2537A in mercury at 4.9 volts is an outstanding example. Rather recently it has been recognized that an exchange of energy between a colliding electron and an atom or molecule may not be followed by a spectral process.[1] This exchange is not restricted by the selection principle whereas the absorption and emission of radiation is thus restricted. The interpretation of a critical potential for which there is no certain and definite emission or absorption line is as yet somewhat in doubt. Some of the critical potentials in mercury vapor reported by Franck and Einsporn[2] are in this category.

The present work was undertaken for the purpose (1) of getting an independent check on the work of Franck and Einsporn with mercury; (2) of determining the principal critical potentials in gallium and indium which have not been previously investigated by the method of

[1] Sommerfeld, Atomic Structure and Spectrum Lines, (Trans. by Brose) 3rd Ed.' Ch. 6, 3, pp. 347.

[2] Franck and Einsporn, Zeits. f. Physik **2**, pp. 18–19 (1920).

[3] Mohler and Ruark, J. Op. Soc. Am. **7**, pp. 819–830 (1923).

electronic impact. Mohler and Ruark[3] have made some measurements with thallium of this group. They report that the potential corresponding to the transition $2p_2-2p_1$ masks all other higher resonance potentials.

Apparatus and Method

Three electrode tube. Preliminary work with mercury and most of the work with gallium and indium was done with this type of tube either in its simple form or as a modification of the Hertz differential tube by making proper electrical connections. Fig. 1 represents the three-electrode tube if we consider only these essential elements: filament F_2, cylindrical grid A, and cylindrical plate B. The filament was platinum, oxide-coated. Electrons were accelerated through a relatively large distance to the cylindrical grid A by a potential V_A and were then retarded through a relatively short distance to a cylindrical electrode B by a retarding potential V_B. Galvanometers G_2 and G_1 were inserted to determine the partial current to B and the total current to A. The electrodes were constructed of nickel. In some of these tubes seals were made with De Khotinsky cement, and in others the seals were made by sealing tungsten wire directly into Pyrex glass. The method of applying the potentials to the electrodes was essentially that shown in Fig. 1 for the Hertz differential tube.

High vacua were produced with all types of tubes by means of a Jones' mercury vapor pump backed by a simple mercury vapor pump, in turn backed by a motor driven rotary oil pump. A mercury gauge was inserted between the Jones' high vacuum pump and the tube under investigation. A tube once baked and highly exhausted could be sealed by means of a trap gauge and communication subsequently established with the high vacuum pump while it was in operation at its highest efficiency. Except in case of accidental breakdown, air was never readmitted to the tube after initial exhaustion and baking. A liquid air trap was inserted between the gauge and tube in the case of gallium and indium.

The Hertz differential tube. (a) *Electrodes and filaments.* Fig. 1 shows the electrode arrangement together with the potentiometer scheme used in applying the potentials. An oxide-coated platinum filament F_1 was used as a source of electrons. This was placed very close to the gauze enclosing one end of the inner cylindrical box A. Electrons were accelerated into the box under various potentials, V_A. The electrons diffused out through the side of box A to the cylinder B (1) under zero retarding potential, (2) under a small retarding potential, V_B, usually 0.1 volt. A shielding electrode C was maintained at earth potential in order to reduce the effect of external stray potentials. The filament F_2 was used to determine ionization potentials by the method of modified space charge. It was sometimes used as the source of electrons when the tube was used as a simple three-electrode tube. It was used as a collecting electrode for positive ions when the tube was used to detect ionization by the Lenard method. Its area would intercept little radiation, and therefore, the results should be little affected by the photoelectric effect.

The electrodes were all made of nickel, B and C from thin nickel sheet and A from nickel gauze of 100 or 150 mesh to the inch. The nickel electrodes were electrically welded to tungsten wires which were sealed directly into the Pyrex tube. The entire tube could be enclosed in a furnace for baking.

(b) *Detection of currents.* The galvanometer G_4 (Fig. 1) was used to determine the constancy of the potentiometer current and also for the

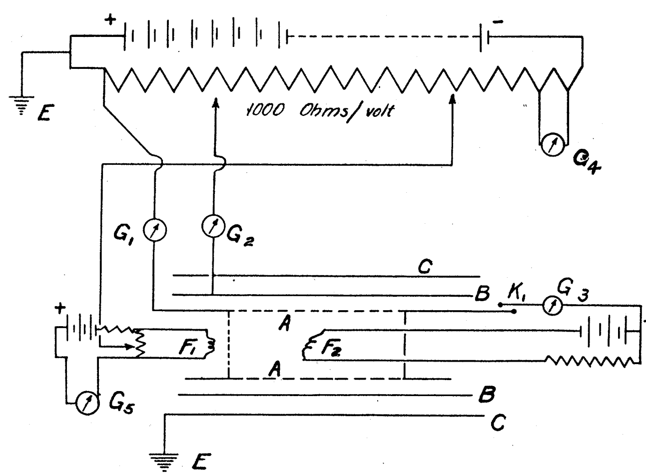

Fig. 1. Arrangement of filaments and electrodes and potentiometer scheme for applying potentials.

detection of ionization by the method of change in gap resistance. A reflecting galvanometer G_5 was inserted in the filament (F_1) circuit and a scale was arranged to receive a spot of light reflected from the mirror of this galvanometer. The scale was so placed as to be under the direct observation of the reader while data were being taken for resonance potentials. The current for F_1 was supplied by two high capacity batteries in parallel and was constant to 1 part in 2000 for several hours. This current was usually of the order of 1.5 amps. The currents as registered by galvanometers G_1 and G_2 were not accepted as trustworthy if there were any indication of a simultaneous change in the galvanometer G_5. Many runs of 10 hours duration were obtained when the filament current was extremely steady and the temperature of the tube constant to within 1° or 2°C. A moderately sensitive Thomson galvanometer G_1 was used to determine the total current from F_1 to box A, while the partial current from A to B was determined by means of a highly sensitive Broca galvanometer. These galvanometers were also used with the simple three-electrode tubes.

(c) *Method used for resonance data.* For a given value of V_A (the accelerating potential) the galvanometers G_1 and G_2 were read, (1) with V_B equal to zero volts (2) with V_B equal to 0.1 volts. The reading of G_2 with V_B equal to zero volts we call R_1 and the reading with V_B equal to 0.1 volt we call R_2. Then $R_1 - R_2$ gives the value of the differential current corresponding to the potential V_A. Thus one point on the differential current-voltage curve is obtained. In most of the work the voltage V_A was increased in steps of 0.1 or 0.2 volts. In this way the data for the resonance curve as shown in Fig. 2D was obtained. In case it was desired to plot the total current curve the reading of galvanometer G_1 was used.

(d) *Method used for ionization data.* The data for the ionization curves shown in Figs. 2A and 2D, and 3F were obtained by the method of modified space charge. To obtain these curves the values of V_A were plotted against the current obtained from the readings of the galvanometer G_3 (Fig. 1). The connections were altered to obtain these data. The connection between G_2 and B was broken, B and A being connected externally, and the key K_1 closed to insert the galvanometer G_3 into the circuit between F_2 and A. Consideration of Fig. 1 will show that the filament F_2 is negative with respect to A. Consequently, electrons would be accelerated toward A and the current registered by G_3 and limited by space charge would remain constant for a constant current through F_2 and for all values of V_A below the ionization potential. This constancy is shown by the flat portions of the ionization curves. When V_A is made large enough that the electrons entering box A have sufficient energy to ionize, then a neutralization of part of the negative space charge in A takes place with the consequence of a sudden rise in the current as registered by the galvanometer G_3. This sudden rise is interpreted as the ionization point. Of course the value of V_A at which this takes place needs correction.

In the Lenard method filament F_2 was maintained negative with respect to all other electrodes and the galvanometer G_2 was connected to it, the battery and galvanometer G_3 being disconnected from F_2. In this method the initial rise in current to F_2 as registered by G_2 so connected was interpreted as the ionization point. (See Fig. 3, curve G, for indium.)

At the ionization point there is a change in the gap resistance between filament F_1 and the electrode A. Since this is a shunt on a part of the potentiometer circuit, the current as registered by the galvanometer G_4 increases since the total resistance in series with the potentiometer battery has decreased. This increase in G_4 was found to be coincident with the sudden increase in G_3 due to the modification of the negative space charge in box A for mercury. Hence, considerable importance has been given to the modification of the gap resistance for the case of gallium and indium in which the other methods of determining the ionization potentials did not give as definite results as had been hoped for.

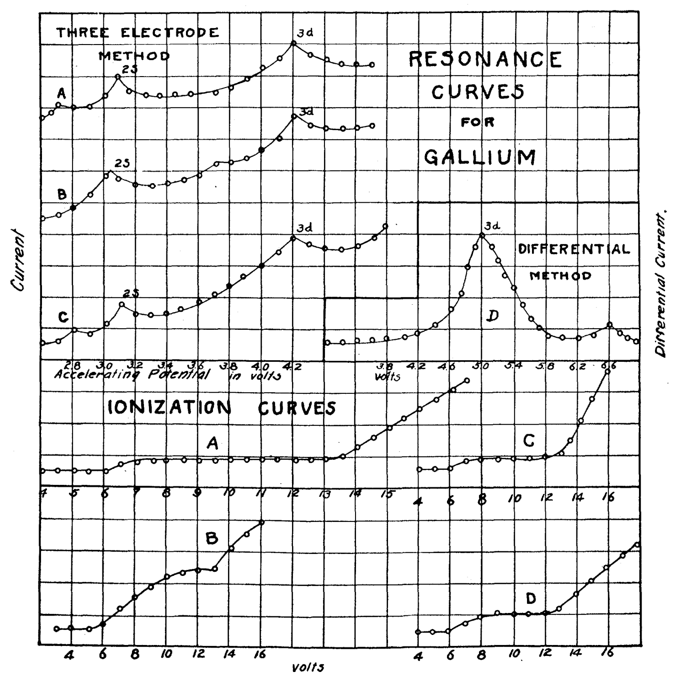

Fig. 2. Curves showing the principal critical potentials for gallium.

(*e*) *Criterion for properly baked tube.* When first exhausted the tubes did not show smooth current potential curves. Baking and pumping was continued until smooth electronic curves were obtained. The vapor to be studied was then admitted and resonance and ionization data secured.

RESULTS

(a) *Mercury.* (*Hertz-differential method.*) The results with this element were reported at the Washington meeting of the American Physical Society (1926), and are given in tabular form in an abstract in the PHYSICAL REVIEW.[4] The results are in general agreement with

[4] Jarvis, Phys. Rev. **27**, pp. 808 (June 1926).

those of Franck and Einsporn, with the addition of several values below 4.68 volts. Work is being continued to determine, if possible, the meaning of the critical potentials found below 4.68 volts. Six such critical potentials have been found. It is thought they may be ascribed to the mercury molecule.

(b) *Gallium.* Typical results for gallium are shown in the various curves given in Fig. 2. Both the gallium and indium used were certified as 98.5 percent pure. Two different tubes were used with this element. Three resonance curves shown in the upper left hand portion of the figure were obtained from the Hertz differential type tube used as a simple three-electrode tube. They show transitions corresponding to the $2s$ and $3d$ levels very decidedly. The other resonance curve was obtained with the other tube used in the differential manner. It shows the transition to the $3d$ level as a pronounced peak. This curve gave but slight indication of the $2s$ level.

The results obtained for ionization are shown by the curves A, B, C, and D in the lower portion of Fig. 2. Curves A and D were obtained by the Lenard method, and B and C were obtained by the modified space charge method. Another curve not shown gave marked evidence of ionization at about 6 volts by the method of change in gap resistance. The curves shown have been corrected for filament drop and velocity distribution by an approximate method. These curves give evidence of a weak type ionization at about 6 volts and a stronger second type ionization at about 13 volts. No evidence was obtained indicating the transition $2p_2-2p_1$.

The results for gallium are summarized in Table I. One critical potential at 1.96 volts was found for which there is no corresponding spectral relation. No interpretation is offered for it.

TABLE I

Critical potentials in gallium.

No.	Critical potentials (volts) from different curves								Mean	Calc.	λ	Series
1	2.20	1.80	1.85	2.10	1.85				1.96		6300	?
2	2.70	2.70	2.60	2.80					2.70	2.96	4172*	$2p_1-2s$
3	3.10	3.00	3.00	3.05	3.15				3.07	3.06	4033*	$2p_2-2s$
4	4.20	4.20	4.52	4.25	4.25				4.22	4.29	2872	$2p_2-3d_2$
	Ionization potentials (volts) from different curves.								Mean	Calc		
Type 1	5.5	5.8	5.5	6.3	6.0	5.8	6.4	5.5	5.80	5.97		
Type 2**	13.0	13.8	12.5	12.8	13.0	13.6	14.0	13.2	13.2			

*4172A and 4033A are "raies ultimes."

** New arc type of ionization.

(c) *Indium.* The various critical potentials found for indium are represented in the curves of Fig. 3. The intermediate portions of the resonance curves *A* and *B* are omitted to facilitate plotting. The latter portions of these curves showing the *3d* level have had the ordinates reduced in order to keep within the allotted space. Curve *A* was obtained with a slightly higher filament temperature than curve *B* and hence the correction is slightly different. Curves *A*, *B*, *C*, and *D* show critical potentials corresponding to transitions to the *2s* and the *3d* levels for indium as decided peaks. The retarding potential applied between electrodes *A* and *B* (Fig. 1) was kept constant at 2.5 volts

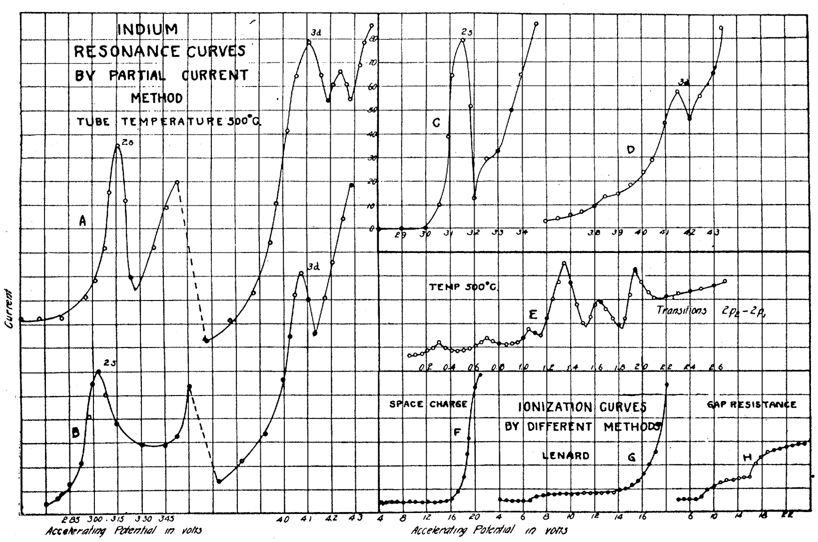

Fig. 3. Curves showing the principal critical potentials for indium.

while data were being taken for curves *A*, *B*, *C*, and *D*. The filament F_1 was shielded with a nickel shield, only the hottest portion being exposed to box *A*. Only a slight correction was necessary. The tube was equivalent to a four-electrode tube in which the two inner grids were at the same potential. Some of the curves show a double peak, the separation being 0.1 to 0.2 volts. This may be due to the transition $2p_2-2p_1$ of either gallium or indium. Curve *E* was obtained with a small retarding potential in order to bring out the transition $2p_2-2p_1$ whose theoretical value is 0.273 volts. The analysis of eight such curves is given in the upper portion of Table II. These results are obtained as differences between recurring peaks on the same curve. The results on ionization are shown by the three curves *F*, *G*, and *H* obtained by the modified space charge, the Lenard, and the gap resistance methods, respectively. Two types of ionization at 6 and 14 volts, approximately, are evident from these curves.

Discussion of Results

(a) *Gallium and indium.* The curves give no evidence of the transition $2p_2-2p_1$ for gallium unless an occasional double peak with 0.1 to 0.2 volt separation could be so interpreted. Spectral considerations place these levels 0.102 volts apart, and it may be that they are too close together to be clearly distinguished by the method of inelastic impact. Foote and Mohler[5] have found a series of recurring peaks at

Table II

Critical potentials in indium.

Transition	Curve No.	Potential (volts) of peaks						Mean diff.
$2p_2-2p_1$	1	0.55	0.85	1.15	1.47	1.75	2.04	0.30
	2	.30	.70	1.06	1.35	1.65	1.93	.32
	3		.77	1.07		1.56	1.85	.26
	4		.60	.89	1.17			.28
	5		.60	.94	1.25	1.55		.32
	6	.34	.65	1.05	1.32	1.62		.32
	7		.65	.95	1.25	1.55		.30
	8	.30	.56	.88	1.15	1.40		.28
						Mean of means		0.297
						Calculated value		.273

Transition	Volt values from different curves							Mean	Calc.
$2p_2-2s$	3.05	2.96	3.00	3.01	3.05	3.15	2.96	3.03	3.01*
$2p_2-3d$	4.05	4.00	4.20	4.05	4.06	4.12	3.97	4.07	4.06**

Ionization	Potentials of breaks				Mean (corr.)	Calc.
Type 1	7.5	8.5	6.7	7.0	6.3 ± 0.5	5.76
Type 2***	15.2	15.4	15.0	14.8	14.1 ± 0.5	

* Corresponding absorption line 4102A.
** Corresponding absorption line 3039A.
*** New arc type of ionization.

0.9 volt apart for thallium agreeing well with the series relation for the $2p_2-2p_1$ transition. The author's value of 0.297 volt is in fair agreement with 0.273 volts based on series relations for the transition $2p_2-2p_1$ in the case of indium. All curves for gallium show the transitions $2p_2-2s$ and $2p_2-3d_2$ and several (see curves *A* and *C* for resonance, Fig. 2) show the transition $2p_1-2s$. Grotrian[6] and Frayne and Smith[7] have shown that for gallium and indium the lines of the series $2p_1-ms$ are absorption lines as well as those of the series $2p_2-ms$. This work is in agreement with theirs but would indicate that the transition $2p_2-ms$ is

[5] Foote and Mohler, Phil. Mag. **37**, pp. 35–50 (1919); also J.O.S.A. **7**, pp. 819–830 (1923).

[6] Grotrian, Zeits. f. Physik **18**, pp. 169–192 (1923); also **12**, pp. 218–231 (1922).

[7] Frayne and Smith, Phys. Rev. **27**, p. 23 (1926).

more probable than the transition $2p_1-ms$. Several curves for gallium (see curve B, Fig. 2) gave evidence of a critical potential at approximately 3.8 volts which corresponds to a wave-length of 3260A. This line is the first member of the series $2p_1-md$ and was found as an absorption line by Grotrian[6] and also by Frayne and Smith.[7] With indium the transitions corresponding to the levels $2s$ and $3d$ came out consistently as well as the transition $2p_2-2p_1$. However, a few curves (not shown in Fig. 3) gave pronounced evidence of the transition $2p_1-2s$ and $2p_1-3d$. The results with both gallium and indium are in fair agreement with the spectral series arrangement. One value for gallium at 1.96 volts has not been reconciled with spectral data. With both gallium and indium the second type of ionization at 12 to 14 volts was found to give the more pronounced breaks in the potential curves. It is thought that the second valence electron is involved at this point. If this be true, then additional spectrum lines should appear at this voltage. Spectroscopic investigation of this point has been undertaken by Frayne and Jarvis[8] for indium. Their results will appear in a later issue of the PHYSICAL REVIEW.

In conclusion the author expresses his gratitude to the Physics Department of Ohio State University where this work was done, and to Dr. Alpheus W. Smith under whose direction and sustaining influence this work was carried out.

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[8] Frayne and Jarvis, PHYS. REV., in press.