

The Electron Affinity of Iodine from SpaceCharge Effects

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The Electron Affinity of Iodine from Space-Charge Effects¹

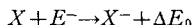
GEORGE GLOCKLER AND MELVIN CALVIN,² *School of Chemistry, University of Minnesota*

(Received September 25, 1935)

The electron affinity of iodine atoms has been determined by a direct method in which only iodine atoms and electrons were involved. The value so obtained is 74.6 k-calories, which is in good agreement with values obtained by other methods. *The concentration of the several ions of different masses (I^- and E^-) have been calculated from their effect on space charge.* It has been established that iodine has no effect on the thermionic emission of tungsten.

I. INTRODUCTION

MANY attempts have been made to determine directly the electron affinity of the elements and to this date comparatively few values have been obtained.³ One of us⁴ has described an empirical method of estimating the electron affinity of the light elements and it is our plan to check these empirical values by experiments in this laboratory. In the present paper we report an experimental determination of the electron affinity of iodine atoms obtained by a new method. We have determined the equilibrium of reaction



at the surface of a hot tungsten filament and from the equilibrium constant we have succeeded in calculating the electron affinity: $-\Delta E_0$. As far as this fundamental principle is concerned it appears that Sutton and Mayer⁵ have employed the same idea and for the same purpose. Since, however, the measurement of the important ratio of the ion to the electron current (I^- to E^-) in our work differs radically from the method used by these authors, we feel that we should present our results. Iodine was used in our study for the reason that its electron affinity is well known and hence any new experimental method can be tested by the use of this element.

II. THEORETICAL CONSIDERATIONS

The equilibrium constant

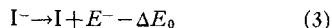
In the case of the ionization of caesium on tungsten Langmuir⁶ was able to measure the equilibrium



established at the surface of a hot filament, where ΔU_0 is the ionization energy derived from spectroscopic data. He obtained very good agreement with the theoretical value of the equilibrium constant calculated by the equation

$$K(Cs, n) = \frac{n(E^-) \times n(Cs^+)}{n(Cs)} = \frac{w(E^-)w(Cs^+)}{w(Cs)} \times \frac{(2\pi m(E^-)kT)^{3/2}}{h^3} \times e^{-\Delta U_0/RT} \quad (2)$$

The $n(x)$ are the concentration of the species " x " in numbers of particles per cc, the $w(x)$ are the statistical weights of the normal states, $m(x)$ are the weights in grams of the individual particles x and the other symbols have their usual meanings. If in our case the reaction occurring at the filament surface is



then

$$K(I^-, n) = n(I) \times n(E^-) / n(I^-) \quad (4)$$

Since the electron affinity is defined for the reverse reaction, we shall write

$$k(I^-, n) = n(I^-) / n(I) \times n(E^-) = 1 / K(I^-, n) \quad (5)$$

and from Eq. (2) we have

$$k(I^-, n) = [w(E^-) \times w(I) / w(I^-)] \times \frac{(2\pi m(E^-)kT)^{3/2}}{h^3} \times e^{-\Delta E_0/RT} \quad (6)$$

¹ Presented at the New York Meeting of the A. C. S. April, 1935.

² This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Melvin Calvin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

³ O. Oldenberg, *Phys. Rev.* **43**, 534 (1933). This paper contains further references.

⁴ Geo. Glockler, *Phys. Rev.* **45**, 111 (1934).

⁵ Sutton and Mayer, *J. Chem. Phys.* **3**, 20 (1935).

⁶ Langmuir, *Phys. Rev.* **43**, 226 (1933).

If, then, $k(I^-, n)$ can be determined experimentally, the electron affinity of iodine can be obtained from Eq. (6). The constant $k(I^-, n)$ can be obtained from Eq. (5) if the concentrations of the interacting species can be determined. $n(I)$ can be obtained from the vapor pressure of iodine assuming that every molecule striking the filament surface is dissociated into two atoms⁵ and the ratio $n(I^-)/n(E^-)$ can be obtained from the space-charge equation. *It is in the determination of this ratio that our method differs from the work of Sutton and Mayer.*⁵ While they employed a magnetron set-up to differentiate between the ion and electron current, we employed the current-potential relations of a space-charge region to evaluate them.

The space-charge equation

The space-charge limited current between a pair of electrodes is given by the well-known Langmuir-Child equation⁷

$$\log i = \log C(e/m)^{1/2} + \frac{3}{2} \log V, \quad (7)$$

where C is a geometrical constant, e/m is the ratio of charge to mass of the carriers of the current and V is the potential difference between the electrodes. By taking current-voltage data in vacuum where electrons only carry the current and plotting $\log i$ against $\frac{3}{2} \log V$ we can determine the geometrical constant C for any experimental conditions. By plotting similar data obtained with iodine present between the electrodes an effective value of e/m can be calculated which will be different from that of the electrons and will depend on the number of other types of charged ions present between the electrodes.

In order to determine the relationship between the effective e/m of Eq. (7) and the number of heavy negative ions (I^-) present we must reconsider the derivation of this equation. It is obtained from Poisson's equation

$$\nabla^2 V = 4\pi\rho, \quad (8)$$

and for cylindrical electrodes:

$$2\pi r\rho = i/u = i(m/2eV)^{1/2}, \quad (9)$$

where ρ is the negative charge density and u is the

velocity of the charged particle: $((2eV)/m)^{1/2}$. Eqs. (8) and (9) yield⁸

$$r d^2 V / dr^2 + dV/dr = (2m/eV)^{1/2} i, \quad (10)$$

which gives on integration from $r=0$ to $r=r$, $(dV/dr)=0$ and $V=0$ at $r=0$:

$$i = 2\sqrt{2}/9r(e/m)^{1/2} V^{3/2}$$

$$\text{or} \quad \text{const} \times V^{3/2} = i(m/e)^{1/2}. \quad (11)$$

In the special case we are considering we shall assume that there are present ions of two masses: $m(E^-)$ and $m(I^-)$. There will be then two currents: $i(E^-)$ and $i(I^-)$ and

$$\rho = \rho(E^-) + \rho(I^-) = i(E^-)/u(E^-) + i(I^-)/u(I^-),$$

or

$$\rho = (1/\sqrt{2}) \{ i(E^-)(m(E^-)/e)^{1/2} + i(I^-)(m(I^-)/e)^{1/2} \} V^{-1/2}. \quad (12)$$

The form of this expression is the same as Eq. (9) with $i(E^-)(m(E^-)/e)^{1/2}$ replaced by $\{ i(E^-)(m(E^-)/e)^{1/2} + i(I^-)(m(I^-)/e)^{1/2} \}$. Since these terms have the same functional relation to V and are subject to the same boundary conditions, the integration will be exactly analogous and we can write the solution directly

$$\text{const} \times V^{3/2} = i(E^-)(m(E^-)/e)^{1/2} + i(I^-)(m(I^-)/e)^{1/2}. \quad (13)$$

Hence the effective value of m/e as determined from experiment is related to its constituents as follows:

$$i(m/e)^{1/2} = i(I^-)(m(E^-)/e)^{1/2} + i(I^-)(m(I^-)/e)^{1/2}, \quad (14)$$

$$\text{and} \quad i = i(E^-) + i(I^-) \quad (15)$$

$$\text{and} \quad \frac{i(I^-)}{i(E^-)} = \frac{m^{1/2} - (m(E^-))^{1/2}}{(m(I^-))^{1/2} - m^{1/2}} = F = \frac{\mu(I^-) \times e}{\mu(E^-) \times e}, \quad (16)$$

where $\mu(I^-)$ is the number of I^- crossing unit area in unit time between filament and plate and $\mu(E^-)$ is the corresponding quantity for electrons.

The equilibrium equation

It is well known from kinetic theory that the concentration of a species is related to the number traversing unit area in unit time, by

⁷ O. W. Richardson, *Emission of Electricity from Hot Bodies* (Longmans, Green & Co., London, 1921).

⁸ Langmuir and Compton, *Rev. Mod. Phys.* **3**, 191 (1931); and Langmuir, *Phys. Rev.* **2**, 450 (1913).

$$\mu(x) = n(x)(kT/2\pi m(x))^{\frac{1}{2}}. \quad (17)$$

The mass of I^- is sensibly the mass of I atom and since the three particles (I , I^- , E^-) are formed at the filament their temperature is the temperature of the filament: T_s . The number of iodine atoms formed at the filament is twice the number of I_2 molecules striking it:

$$\mu(I_2) = P(I_2)/(4\pi m(I)kT_G)^{\frac{1}{2}}, \quad (18)$$

where $P(I_2)$ is the pressure of iodine molecules in baryes and T_G is the temperature of the iodine gas (about room temperature). The equilibrium constant (Eq. (5)) can now be written:

$$k(I^-, n) = \frac{Fk}{P(I_2)} \times \left[\frac{m(I)T_G}{2m(E^-)} \right]^{\frac{1}{2}} \times T_s^{\frac{1}{2}} \times \frac{3 \times 10^{-10}}{4}, \quad (19)$$

and combined with Eq. (6) permits the calculation of the electron affinity.

III. EXPERIMENTAL PROCEDURE

The experimental set-up is shown in Figs. 1 and 2 and consists of a diode (filament and plate) with an iodine reservoir. The filament is a tungsten wire 0.1 mm thick and about 42 mm long. The plate is made of tantalum (0.152 mm thick) and is in the form of a cylinder 45 mm high and 21.4 mm diameter. The glass tube is 35.6 mm in diameter. The details of the electrical connections are shown in Fig. 1. The experimental set-up is essentially that used by Heinze⁹ in measuring the work function by the cooling method. It is a Wheatstone bridge with audio-frequency current for balancing and direct current for heating the filament which forms one of the arms of the bridge. The various parts of the electrical arrangement are:

- A_m , ammeter measuring approximately the current through the bridge.
- A, B , endcoils of Leeds and Northrup Kohlrausch bridge each having a resistance of 124.14 ohms.
- C_1 , blocking condenser having a capacitance of about one mf.
- C_2 , variable condenser having a range of 0.00003–0.04 mf. It is necessary to balance out any capacitance that might be introduced into the bridge by the experimental tube or at other points.
- E_1 , experimental tube.

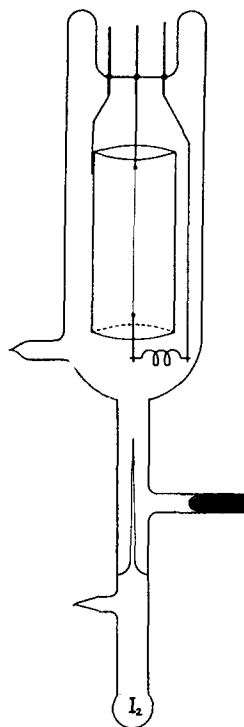


FIG. 1. Reaction tube.

- F_1 , parallel resonance circuit tuned to the frequency of the oscillator and thus providing an infinite impedance to the audiofrequency attempting to get through the plate circuit and preventing this auxiliary current from falsifying the bridge measurements.
- F_2 , the filament of the experimental tube.
- I , manganin slide wire in mercury (10 ohms).
- K , slide wire of Leeds and Northrup Kohlrausch bridge (type 54161). Its resistance was checked on a standard bridge of the Physics Department and is 27.72 ohms.
- L_1 , lead storage "B" batteries.
- L_2 , set of four two hundred-ampere hour lead storage cells. They could be arranged in any series or parallel combination so as to deliver up to 24 volts. It is very essential that these batteries be capable of maintaining a current of about 1.5 amperes steady to within 0.005 ampere over a period of one hour.
- M , manganin slide wire in mercury (one ohm).
- $M.A.$, microammeter with shunts capable of measuring currents from 2×10^{-7} – 3×10^{-2} amp. It measures the plate current.

⁹ Heinze, Ann. d Physik **16**, 41 (1933).

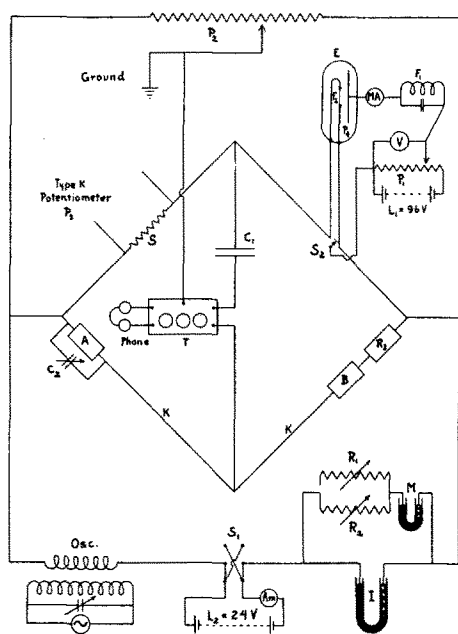


FIG. 2. Electrical connections.

- Osc., vacuum tube oscillator which supplies the audio-frequency current to activate the bridge.
- P₁, potentiometer (2700 ohms).
- P₂, potentiometer (10,000 ohms) used as a Wagner ground on the bridge.
- P₃, type "K" Leeds and Northrup potentiometer across the standard resistance "S." It is used to make the critical measurement of the current through the filament.
- P₄, the plate of the experimental tube.
- R₁, variable resistance (100 ohms) for controlling the current through the filament.
- R₂, variable resistance (25 ohms).
- R₃, standardized three-dial noninductive resistance (999 ohms). It is necessary in order to achieve a balance when the end coils are in.
- S₁, one-ohm Leeds and Northrup standard resistance.
- S₂, reversing switch for reversing the current through the bridge.
- S₃, arrangement for connecting the negative terminal of the "B" battery to either end of the filament.
- T, three-tube amplifier with telephone used as the balance detector of the bridge.
- V, voltmeter for plate voltage.

The tube was outgassed by standard procedure and the work function of tungsten was determined by two methods.

The work function of tungsten

The work function of the filament material (tungsten) was obtained from the temperature variation of the saturation current by the use of well-known relations. The object was to ascertain that the filament surface was clean. The value for the work function was found to be 4.59 electron volts which is in very close agreement with the accepted value for pure tungsten. The second method employed was a measurement of the cooling effect on the filament due to the evaporation of the electrons. The value obtained is 4.60 electron volts in excellent agreement with the value obtained from the Richardson equation. The temperature of the filament was obtained from the heating current and the Langmuir table.¹⁰

These measurements established the following facts: (1) The apparatus will actually measure heat values at the surface of the filament. (2) The methods used in the measurements of the various experimental quantities and the estimated corrections (for example end losses etc.) are valid. (3) The material of the filament is satisfactory, i.e., clean. (4) The tube is free from residual gases.

Admission of iodine

The tube having been prepared by outgassing and filament-aging was then filled with iodine vapor. After the iodine was admitted the filament was again allowed to age for at least thirty hours, always keeping liquid air on the tube containing the solid iodine supply. At this point the filament was subjected to the emission test and it was found to be unaltered. Moreover raising the iodine pressure even as high as 10^{-4} mm Hg had no effect on the saturation emission characteristics of the filament. This seems entirely reasonable for before a molecule can affect the thermionic emission from a surface it must be adsorbed on the surface. At our high filament temperatures (above 2000°K) iodine atoms are not adsorbed. This finding is in agreement with the work of Van Pragh¹¹ who studied the accommodation coefficient of helium on platinum which had been subjected to various treatments in iodine. He found that platinum treated in

¹⁰ Langmuir and Jones, Gen. Elec. Rev. 30, 310-9 (1927).

¹¹ Van Pragh, J. Chem. Soc. 798 (1933).

iodine above 1650°K showed an accommodation coefficient toward helium corresponding to that of a clean surface. But when iodine was allowed to come into contact with the platinum at any lower temperature, the accommodation coefficient changed immediately to that of a platinum surface covered with a layer of iodine. Since tungsten iodide is much less stable than platinum iodide it seems reasonable to say that at our high temperatures *iodine has no effect on the thermionic emission from tungsten*. This is in agreement with statements made by Langmuir in private communications to others.¹²

But it still remains true that the presence of the iodine vapor between the electrodes can and does influence the plate current. In the space-charge limited region and below the ionization potential of iodine (molecule or atom) the current is affected by the creation of heavy negative ions (I^- etc.) which help to increase the negative space-charge density and thus decrease the electron current. As soon as the ionization potential is reached positive ions are formed, the negative space charge is neutralized and the plate current jumps above its value in a vacuum. If the number of positive ions is large enough the saturation current may even be larger than that in a vacuum.

Current-voltage relation in iodine

The data needed for the calculation of the electron affinity are simply a set of current-voltage tables taken in the space-charge limited region and at voltages less than the ionization potential of iodine. This information together with the temperature of the filament, the pressure of the iodine at which the measurement was taken and the gas temperature is all that is needed for the calculation of the electron affinity.

The filament temperature is first set with liquid air on the iodine supply. The Wheatstone bridge in which the filament is located is balanced and the plate current is measured as a function of plate voltage. The iodine is then admitted to any desired pressure by warming the side tube in the proper bath. The filament will cool off because of the thermal conduction of the iodine vapor.

¹² Van Praegh and Rideal, Proc. Roy. Soc. A134, 385 (1931), and reference 5.

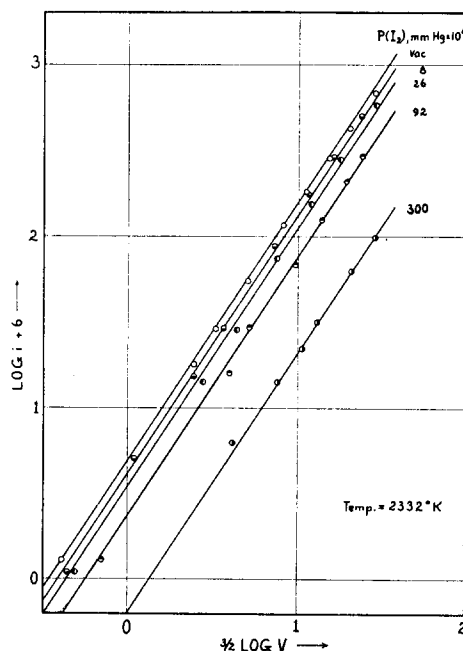


FIG. 3. Current-voltage relations in iodine.

This cooling effect causes a drop in resistance of the filament which will become apparent on the Wheatstone bridge. *By increasing the filament heating current so as to reestablish the filament resistance originally found in a vacuum, we assume that the filament temperature is returned to its original value.* Again we find the plate-current as a function of plate voltage under the new conditions and repeat the procedure for several pressures of iodine. For each filament temperature a new set of vacuum data must be taken. A sample run is shown in Table I. The filament temperature is 2332°K. The data are plotted in Fig. 3.

IV. DISCUSSION OF RESULTS

The current ratio F

The data given in Table I and shown in Fig. 3 are used to calculate effective values of m which satisfy the Langmuir-Child equation under any given set of conditions and hence the value of F the ratio of the current carried by the iodide ions

TABLE I. Current-voltage relation in I_2 , filament temperature $2332^\circ K$.

IODINE TEMP. & PRESSURE ($^\circ C$ & mm Hg)	PLATE CURRENT (amp. $\times 10^6$)	PLATE VOLTAGE (volts) V	IODINE TEMP. & PRESSURE ($^\circ C$ & mm Hg)	PLATE CURRENT (amp. $\times 10^6$)	PLATE VOLTAGE (volts) V
$-180^\circ C$ ($< 10^{-6}$)	1.3	0.55	$-31.0^\circ C$ 0.0008	1.1	0.58
	5.1	1.06		15.4	1.82
	17.9	1.82		29.4	2.38
	28.9	2.22		89.0	3.76
	55.0	2.95		176.0	5.08
	117.0	4.06		293.0	6.38
	184.0	5.01		510.0	8.17
	288.0	6.15	$-21.1^\circ C$ 0.0026	1.1	0.62
	430.0	7.38		14.2	1.98
	690.0	9.34		29.1	2.67
$-40^\circ C$ 0.00018	1.9	0.72		75.0	3.84
	15.7	1.73		156.0	5.23
	27.4	2.22		283.0	6.78
	87.0	3.63		590.0	9.34
	179.0	5.00	$-10.45^\circ C$ 0.0092	1.3	0.79
	282.0	6.13		16.0	2.51
	610.0	8.82		29.5	3.23
				69.0	4.55
				125.0	5.75
				211.0	7.16
				295.0	8.25

(I^-) and the electrons (E^-). From Eq. (7) we see that the intercept on the $\log i$ -axis of Fig. 3 gives the constant $C(e/m)^{1/2}$. The straight line referring to the conditions in a vacuum shows of course the relation when electrons only are carrying the current. Hence e/m is that of the electron ($4.774 \times 10^{-10} \times 6.06 \times 10^{23} \times 1845 \times 1.008^{-1} = 7.27 \times 10^8$). For the case shown in Fig. 3 we find for a vacuum

$$\log C(e/m)^{1/2} = 0.66 - 6.00 = 4.66 - 10,$$

$$\text{and } C(e/m)^{1/2} = 4.57 \times 10^{-6}$$

$$\text{hence } C = 4.57 \times 10^{-6} / 7.27 \times 10^8 = 6.28 \times 10^{-15}$$

in units where electric charge is in electrostatic units and masses in weights of atoms in grams. With iodine in the tube at a pressure of 9.2×10^{-3} mm Hg we find the straight line $\log i$ vs. volts to intersect the $\log i$ axis at a point

$$\log C(e/m)^{1/2} = 0.33 - 6 = 4.33 - 10$$

$$\text{or } C(e/m)^{1/2} = 2.14 \times 10^{-6}.$$

Using the value of C found above we obtain

$$(e/m)^{1/2} = 2.14 \times 10^{-6} / 6.28 \times 10^{-15} = 3.41 \times 10^8.$$

Considering the carriers singly charged we use

$$e^{1/2} = (4.774 \times 10^{-10})^{1/2} = 2.19 \times 10^{-5}$$

$$\text{and } e^{1/2} / (e/m)^{1/2} = m^{1/2} = \frac{2.19 \times 10^{-5}}{3.41 \times 10^8} = 6.43 \times 10^{-14}.$$

We need to know

$$(m(E^-))^{1/2} = [1.008 / (1845 \times 6.06 \times 10^{23})]^{1/2} = 3 \times 10^{-14}$$

$$\text{and } (m(I^-))^{1/2} = [127 / (6.06 \times 10^{23})]^{1/2} = 1.45 \times 10^{-11}$$

in order to evaluate F from Eq. (16):

$$F = \frac{6.43 \times 10^{-14} - 3.0 \times 10^{-14}}{1.45 \times 10^{-11} - 6.43 \times 10^{-14}} = 2.37 \times 10^{-3}.$$

This procedure is repeated for each iodine pressure, a new geometrical constant being determined at each filament temperature.

Calculation of electron affinity

Eqs. (6) and (19) can be used to calculate the electron affinity. The following values of constants appearing in the equation were used: The statistical weight of the electron $w(E^-)$ is 2; the normal state of the iodine atom is $^2P_{3/2}$ and hence $w(I) = 4$ and for the iodine ion the ground state is S_0 giving $w(I^-) = 1$; $k = 1.371 \times 10^{-16}$; $m(E^-) = 9 \times 10^{-28}$; $h = 6.55 \times 10^{-27}$; $m(I) = 20.94 \times 10^{-23}$; $T_0 = 300^\circ K$; $e = 2.71828$. The final equation becomes

$$-\Delta E_0 = 4.575 (\log F + 2 \log T_0 - \log P(I_2) + 1.075). \quad (20)$$

The results of our experiments are summarized in Table II. The measurements extend over a

TABLE II. Electron affinity of iodine.

EXPERI- MENT No.	FILAMENT TEMPERATURE T_f ($^\circ K$)	IODINE PRESSURE $P(I_2)$ (mm Hg $\times 10^3$)	CURRENT RATIO F ($\times 10^4$)	ELECTRON AFFINITY $-\Delta E_0$ (k-calories)
1	2400	8.50	2.12	79.2
2	"	2.80	3.45	75.7
3	2395	3.78	4.00	75.1
4	"	30.00	27.50	74.2
5	2332	0.18	1.03	80.5
6	"	0.80	3.65	79.3
7	"	2.60	8.22	77.8
8	"	9.20	23.70	76.7
9	"	30.00	71.80	75.4
10	2031	3.15	12.21	67.7
11	"	30.00	87.70	66.6
12	2020	0.85	106.2	72.0
13	"	2.70	163.5	69.2

average: 74.6 kcal.

temperature range of 380°K and involve a 166-fold change in iodine pressure.

Concluding remarks

In the development of the relation between the effective mass of the carriers of electricity (m) and the ratio (F) of ion to electron current we assumed that there were present only two kinds of ions: I^- and E^- . The possibility of the formation of heavier negative ions I_2^- and I_3^- immediately arises. Should these ions exist in the tube in quantity, then the F values would be two large and hence result in high values of $-\Delta E_0$. Since the average value obtained for the electron affinity is apparently not too high, we conclude that our original assumption is correct. This is further supported by the work of Hogness and Harkness¹³ who have shown that in the low voltage arc in iodine, the only result of a primary process is I^- and that I^- is the result of the only primary process. They have shown that I_2^- and I_3^- exist only in very small quantity and that they arise by secondary processes after I^- has been formed.

Another assumption that was made in obtaining the equilibrium equation, is that every iodine molecule that strikes the surface of the filament is dissociated. This is also justified by the results obtained. Langmuir in a private communication to others⁵ has stated that such is the case. It should also be noted that the heat of dissociation of iodine is only 1.5 electron volts.

¹³ Hogness and Harkness, *Phys. Rev.* **32**, 784 (1928).

The work of Stark and Bodenstein¹⁴ indicates that iodine vapor at low pressure would be almost completely dissociated at 1200°C. The filaments used were all above 2000°K and since it is reasonable to assume that the filaments used are not perfectly smooth so that each molecule has a very good chance to approach temperature equilibrium with the filament, it is to be expected that almost every molecule striking the surface will be dissociated. There is only one piece of evidence to the contrary. Van Pragh and Rideal¹⁵ in their experiments on the attack of platinum and tungsten by the halogen vapors come to the conclusion that the dissociation even at our high temperatures is given by

$$\mu(I) = 2\mu(I_2) \times e^{-D/RT} \quad (21)$$

where D = dissociation energy of iodine molecules. No explanation for this discrepancy has been suggested. In our work it may be assumed that the results indicate complete dissociation of every iodine molecule striking the hot filament.

The possibility exists that the electrons suffer reflection at the filament surface. This situation has already been discussed by Sutton and Mayer.⁵ Our experiments are not accurate enough to shed light on this point. From the results obtained it may be seen that the various assumptions made must be reasonably correct, since the value of electron affinity found checks the results of other methods satisfactorily.

¹⁴ Stark and Bodenstein, *Zeits. f. Elektrochemie* **16**, 961 (1910).

¹⁵ Van Pragh and Rideal, *Proc. Roy. Soc.* **A134**, 385 (1931).