A Direct Experimental Determination of Electron Affinities, the Electron Affinity of Iodine

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By observing the ratio of the negative ion emission to the electron emission from a thermionic surface of known temperature in an atmosphere of electronegative molecules of known pressure the electron affinity of the atoms can be calculated. A magnetron set up has been used to distinguish electron and ion currents. With a tungsten filament at about 2000°K, and an iodine atmosphere of about 1 micron pressure, the electron affinity of iodine atoms has been found to be 72.4 ± 1.5 kcal.

INTRODUCTION

THE measurement of the electron affinity of gaseous electronegative atoms has been for some time a problem of considerable interest, but no generally satisfactory method of attack has as yet been evolved. Attempts to observe the recombination spectra[1] or the absorption spectra limit of the free ions[2] have always failed due to the low intensities obtained.

Theoretical calculations[3, 4] and experimental measurements[5, 6] of the lattice energies of the alkali halides enable the calculation of the electron affinities of the halides, the results of which are undoubtedly of considerable accuracy, but this method is not only indirect but is also of limited applicability.

The method described here, and used on iodine, appears, with slight modifications to be of very general applicability. It is direct and simple. It is, however, subject to one difficulty of interpretation which detracts considerably from the certainty of the results. This point will be discussed at the end of this section.

The electron affinity of an atom is the negative of the energy change, ΔE_0 at absolute zero of the reaction (1),

$$X_{gas} + e^-_{gas} \rightarrow X^-_{gas}. \qquad (1)$$

The method presented here for measuring this quantity is based on the following considerations: Regard any surface in temperature equilibrium at a temperature T_s with a gas phase containing atoms, X, ions, X^- and electrons, e^-. Since equilibrium exists the numbers of each atom species, 'a,' striking unit surface per unit time from the gas phase must be equal to the numbers leaving the surface. The numbers striking, and therefore the numbers leaving, unit surface per unit time, Z_a, bear a simple relation (2) to the equilibrium pressure, P_a, in the gas phase and therefore to the equilibrium constant, K, and to the standard free energy change, ΔF, of reaction (1).

$$Z_a = P_a / (2\pi m_a k T_s)^{\frac{1}{2}}, \qquad (2)$$

$$K = e^{-\Delta F/RT_s} = \frac{P_{x^-}}{P_x \cdot P_{e^-}} = \frac{Z_{x^-}}{Z_x \cdot Z_{e^-}} (2\pi m_{e^-} k T_s)^{\frac{1}{2}}, \qquad (3)$$

where T_s = temperature of equilibrium, m_a = mass of particle "a," k = Boltzmann's constant.

Now if the reflection coefficient of the surface for each species is zero, that is, if each atom striking from the gas phase remains long enough on the surface so that its chance of leaving as an ion is the same as if it had been an ion when it struck, and if each electron striking the surface has the same chance of any particular future as if it had struck in combination with an X atom as an ion, then the ratios of the numbers leaving the surface will be independent of the existence of equilibrium in the adjacent gas phase. If this is the case, and we have quasi-equilibrium between the gas and surface phases, i.e., if the gas phase contains only cold X atoms, or even

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[1] J. Franck, Zeits. f. Physik 5, 428 (1921).
[2] Angener and Müller, Zeits. f. Physik 26, 643 (1925).
[3] See Max Born, *Probleme der Atomdynamik.*, Berlin, Julius Springer, p. 150 (1926).
[4] J. E. Mayer and L. Helmholz, Zeits. f. Physik 75, 19 (1932).
[5] J. E. Mayer, Zeits. f. Physik 61, 798 (1930).
[6] L. Helmholz and J. E. Mayer, J. Chem. Phys. 2, 245 (1934).

only cold X_2 molecules at a temperature $T_G < T_s$, but the total mass of X leaving the surface as molecules, atoms, or ions is equal to the total mass striking the surface, say only as X_2 molecules, then the relative numbers of ions, atoms and electrons leaving the surface still enable the calculation of the equilibrium constant in the gas phase and of the standard free energy change of reaction (1).

In the special case that the temperature is so high and the pressure so low that almost complete dissociation of X_2 into X is called for, and if $Z_x - \ll Z_x$ we may write $Z_x = 2Z_{x_2}$, where Z_x gives the number of atoms leaving unit surface per unit time, and Z_{x_2} the number of molecules striking. For Z_{x_2} the relation (2) holds, and remembering that $m_{x_2} = 2m_x$ we obtain in place of (3)

$$e^{-\Delta F/RT_s} = \frac{Z_x-}{Z_e-} \cdot \frac{1}{P_{x_2}} \left(\frac{T_G}{2T_s} \frac{m_x-}{m_e-} \right)^{\frac{1}{2}}$$

$$= \frac{i_x-}{i_e-} \cdot \frac{1}{P_{x_2}} \left(\frac{T_G \cdot m_x-}{2T_s \cdot m_-} \right)^{\frac{1}{2}}. \quad (4)$$

In the last part of (4) use is made of the fact that the ratio of the numbers of electrons and ions leaving the surface is equal to the ratio of the current carried by the electrons, i_e-, to that carried by the ions, i_x-.

From the measurements of P_{x_2}, i_e- and i_x-, ΔF may be evaluated (Eq. (4)), and from this by the simple calculation indicated in Eq. (5) the electron affinity, $-\Delta E_0$.

$$\Delta F = \Delta H - T_s \Delta S = \Delta E_0 + \int_0^{T_s} \Delta C_P dT - T_s \Delta S, \quad (5)$$

where ΔH, ΔS and ΔC_p have the usual significance. Since reaction (1) involves only monatomic gases, and since the temperature T_s is always so low that the internal energy is either negligible or may be readily calculated, the evaluation of ΔS and ΔC_P is easily made.

Thus one is able to determine the electron affinity of X through observation of the current i_e- and i_x- carried by the electrons and ions, respectively, leaving a heated surface of known temperature T_s in an atmosphere of X_2 molecules at known pressure P_{x_2}. The currents i_e- and

i_x- may be readily measured independently of one another by magnetic removal of the electron current.

One assumption only is made, namely that there is zero reflection coefficient at the heated surface for all atomic species.

Regarding this assumption little can be said of an absolutely conclusive nature. It is known that iodine molecules dissociate completely to atoms on a hot tungsten filament,[7] and also that caesium atoms lose electrons completely on contact with a surface of high work function.[8]

The experiments here reported cover a 130°K range of temperature and a fourteenfold range of iodine pressure, in which range the apparent work function of the tungsten filament changed by 0.4 volt and differed by almost 1 volt from the true work function of clean tungsten, probably showing varying degrees of coating of the filament. In this range the calculated electron affinity showed no trend, indicating a constant reflection coefficient; a rather remarkable circumstance if the reflection coefficients were not essentially zero. It is to be emphasized here that a 10 percent reflection coefficient would introduce an error of only $RT \ln 1.1$ or about 0.4 kcal. in the calculated electron affinities, a 50 percent reflection coefficient, on the other hand, would introduce a very appreciable error of 2.7 kcal.

A temperature and surface independent reflection coefficient for electrons of exactly $\frac{1}{2}$ may possibly exist, as indicated by the fact that there is a twofold discrepancy in the thermionic emission constant for electrons as obtained by experiment and as calculated by modern theory.[9] The calculation of electron affinities according to Eq. (4) assumes tacitly that the theoretical electron emission equation is correct, and that the experimental discrepancy is due to some such phenomenon as a temperature dependent work function. Should subsequent investigations of the theory of electron emission indicate that there does exist a reflection coefficient of $\frac{1}{2}$ for electrons on metal surfaces (as would be obtained if image forces were neglected in the

[7] Personal communication from I. Langmuir.
[8] Langmuir and Kingdon, Proc. Roy. Soc. A107, 61 (1925). Kingdon, Phys. Rev. 21, 510 (1924).
[9] See for example S. Dushman, Rev. Mod. Phys. 2, 381 (1930).

original calculation), then the values of electron affinities reported in this paper should all be raised by about 2.7 kcal.

APPARATUS

The apparatus finally evolved for the purpose of measuring ion and electron currents under the conditions outlined above consists in the electron tube shown in simplified form in Fig. 1 and described below.

A vertically suspended filament, F, which can be electrically heated and whose temperature, T_s, may be accurately determined, is closely surrounded by a cylindrical grid, G, concentric with it; G being in turn surrounded by the concentric plate P of such size that the radius of G is approximately one-third that of P. The whole tube is surrounded on the outside by the solenoid S concentric with F. By a suitable electrical system G and P may be maintained at the potentials V_G and V_P, respectively, with $V_P > V_G > 0$ and with $V_F = 0$; by means of the galvanometer, E, connected in series with F, current flow to the plate may be detected.

If now this tube is filled with X_2 vapor at a definite pressure and the filament temperature raised to a determined value, equilibrium (1) will exist on the surface of the latter and, according to the previous considerations, X^- ions and electrons will be emitted. Both ions and electrons travel radially in straight lines to the plate where they are collected and recorded as a galvanometer deflection, Δ_{e^-}, moreover since $Z_{X^-} \ll Z_{e^-}$ this deflection may be considered as due to only the electrons and hence i_{e^-} is simply calculated from Δ_{e^-}.

If now a current is passed through the solenoid the tube operates as the familiar magnetron set-up and the electron current is prevented from reaching the plate P. In high vacuum ($<10^{-6}$ mm) the electron current to P may be completely (to less than the 10^{-6} part of its original value) eliminated by solenoid currents about 4 times greater than that theoretically necessary to deflect the electron beam into a circle of diameter equal to the radius of the plate P. In the presence of an inert gas (Hg vapor at 2×10^{-3} mm) a slightly higher solenoid current (5 or 6 times the theoretical) is necessary to eliminate the

electron current to P. These solenoid currents, however, have no appreciable effect on the current due to the heavy ions, and thus ion currents i_{X^-} as well as the electron current i_{e^-} may be independently determined under fixed conditions of P_{z_2} and T_s.

Details of construction of the electron tube used in the measurements on iodine together with its electrical circuit are shown in Fig. 2.

The tube itself consists of two parts, the body, A, which also acts as a plate support, of Pyrex glass shaped as shown and the grid-filament support and leads sealed in the Pyrex cap, C. This cap fits on A and is united with it by sealing, thus affording a vacuum-tight joint free from grease which is easily opened for repairs. In addition, A is fitted with an exhaust tube, Q, by means of which evacuation is accomplished.

The collecting plate B (4.75 cm diam., 6.75 cm long) fits snugly into supports in A and
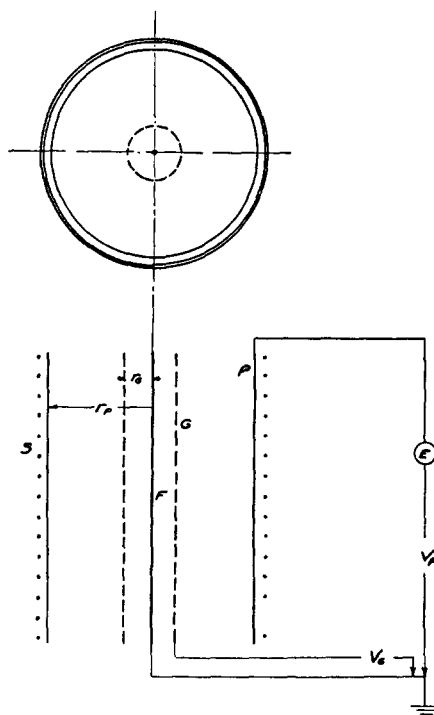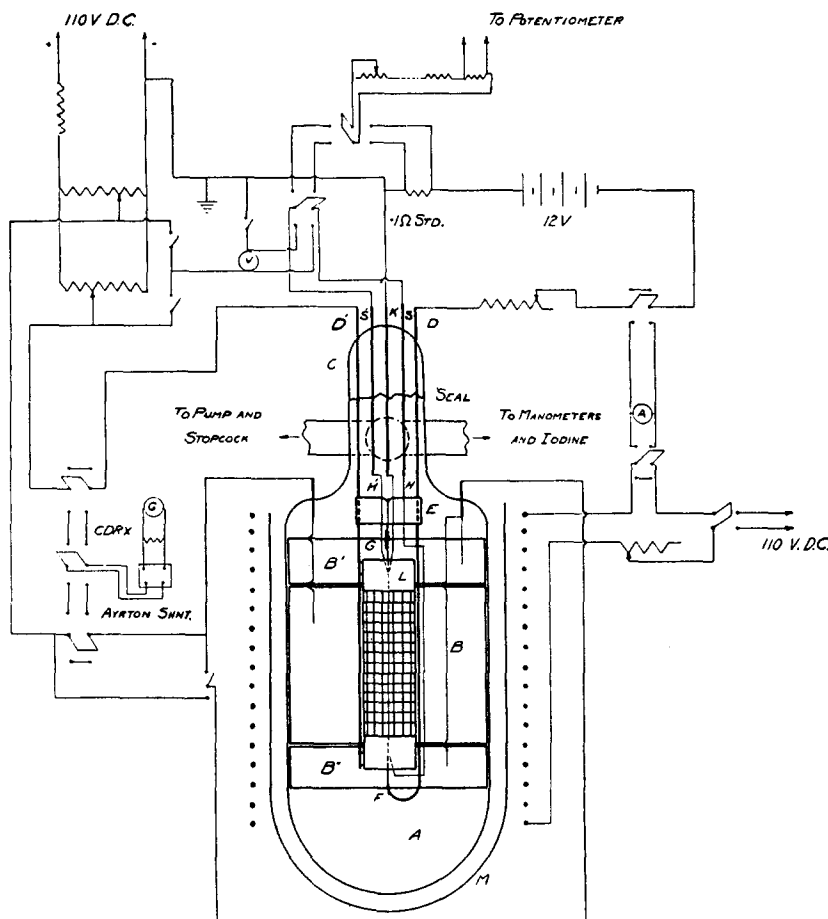

FIG. 1.

Fig. 2.

between the guard plates B' and B'' at a distance of 1.5 mm from each. These plates are of Monel sheet bent into cylindrical form and welded; electrical contact is made with them by tungsten wires sealed through the tube shoulders. (B is in the galvanometer circuit during all measurements of plate current, B' and B'' are connected in series, charged to the same potential as B but not in the galvanometer circuit, their purpose being to prevent the registering of stray currents and to insure uniformity of the electrical field.)

The grid-filament holder is built up around the two tungsten rods D, D' (2.1 mm diam.) sealed

in the cap C as sketched, the rods serving in addition as electrical leads. For support D and D' are fused in the glass block E, and D' has welded at its lower end the Monel filament clamp F.

The filament of General Electric pure tungsten wire (8.77 cm long, 0.019 cm diam.) is supported as indicated by the helical tungsten spring, G, hung from F, serving to keep it taut and in position even at white heat. A flexible nickel wire welded to K constitutes the second filament lead. Exactly at the extreme ends of the filament are welded two fine nickel wires II and II' which

connect to the short tungsten rods S and S' and enable the potential drop across the filament itself to be accurately measured.

The grid L (6.28 cm long, 1.25 cm diam.) welded to D is of Monel gauze (25 mesh) and is fitted at either end with solid rings M and M' (1.61 cm long). Such an arrangement allows charged particles from only the central portion of the filament to reach the plate through the grid, thus assuring that all of the latter registered as a plate current shall have come from a region of uniform temperature. Both grid and filament are so adjusted as to hang in the center of the tube.

Finally all exposed parts of the rods D, D', S, S' and K are sealed in Pyrex to cut down gas evolution on heating.

The body of the tube is surrounded by the cylindrical Pyrex jacket, M, through which cooling water can be continually passed. This cooling eliminates plate heating through filament radiation and serves the double purpose of retarding gas evolution and preventing electrical leakage.

Through Q connection is made to a simple high vacuum line activated by a two stage Pyrex mercury diffusion pump with the necessary backing and containing a carefully calibrated McLeod gauge accurate in the range from 1.0×10^{-5} to 5×10^{-3} mm. To protect the tube from back diffusion of mercury vapor and stopcock grease (Apiezon "L" was used) several liquid air traps of the usual variety were placed in the line at strategic points, the last of these being separated from the tube by the greaseless stopcock as illustrated in Fig. 2A. This was of the type that contains a small glass encased iron bar and is operated magnetically and had been particularly well ground; it would hold, against a flat vacuum, pressures of 10^{-3} mm for

FIG. 2A. Magnetic stopcock.

thirty minutes without noticeable leakage. Thus one was enabled by closing this valve to build up pressure of condensable gases to this order of magnitude in the tube independently of the trap temperatures. In order that the pressure in the tube under these conditions might be measured connection is also made through Q with two quartz fiber manometers. One of these was of the ordinary bent loop style, the other being in the form of a bent loop with a small hollow Pyrex ball sealed at the apex. The ball served to increase the period of the fiber, but made reading the manometer much more rapid and trustworthy and satisfactory at higher pressures. Both manometers were calibrated with a great deal of care against the McLeod gauge in various pressures of air, the fact that the calibration curves were accurately linear indicating the latter to be essentially correct. In order to be doubly certain on this point a pressure of mercury vapor was allowed to build up in the system through the warming of the liquid air traps. From the temperature of the system this pressure could be accurately calculated and using the manometer calibration curve it could be determined experimentally; the two values agreed to within 0.1 micron. In practice it was found that measures of the same pressure carried out on the two manometers never differed by as much as 10.0 percent.

The iodine used in this investigation was prepared in ampules as described below and stored in an ampule holder sealed to Q. Iodine as needed was admitted to the evacuated system through breakage of the individual containers by a small magnetic hammer and was distilled into and retained in a special trap in the line.

Thus concluding the description of the vacuum system, there remain only a few remarks to be made regarding the electrical circuit. In order to determine precisely the temperature of the filament from its volt-ampere characteristics it was necessary to measure accurately the potential drop across the filament and the current flowing through it. The first of these was carried out directly with the potentiometric set-up indicated, the second indirectly as the potential drop across a standard 0.1 ohm resistance. In this manner observations could be obtained accurate
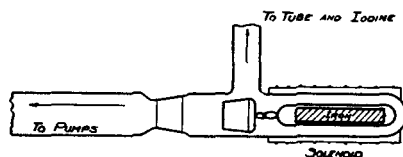
to 1.5 percent (an accuracy of 10°K in the measurement of T_s), the high resistances in the potentiometer circuit insuring that the current flow through the latter be less than 0.01 of the total.

The solenoid consisted of three windings of enameled copper wire (B.S. gauge No. 24) or fifty-four turns per centimeter on an insulated brass tube and was 7.6 cm in diameter and 24.2 cm long. It was, in addition, water-cooled to prevent variations in the field strength due to temperature increase of resistance. The magnetic field produced by it in the electron tube was not uniform for two reasons: first no account was taken in regard to proper orientation in the earth's magnetic field and second there was an inhomogeneity produced due to the end effect— the deviations from uniformity are small, however, and for our purpose are not important.

The galvanometer used was a Leeds and Northrup HS type having as set up a sensitivity of 5.72×10^{-11} amp./mm; equipped with the Ayrton shunt shown, currents as high as 1.0 $\times 10^{-3}$ amp. could be measured on it. Finally the whole electrical circuit was carefully insulated by sealing on wax blocks so that under running conditions any electrical leak which may have existed was undetectable as a galvanometer scale deflection.

MEASUREMENTS

Both the iodine used and the vacuum line were specially treated. The former was Baker's best C.P. reagent grade and was subject to a triple fractional distillation in a well baked vacuum system under constant pumping with a view to removing chemical impurities such as chlorine and bromine and to the elimination of occluded gases. The accomplishment of this last appeared very difficult since even after long pumping there was still a slight residue of non-condensable gases evolved on vaporizing the iodine; past a certain point pumping seemed to have no affect toward remedying this condition. Since, however, this evolution was never responsible for a pressure in the system of greater than $1.0\text{-}2.0 \times 10^{-4}$ mm it was practically negligible for the purpose at hand. The iodine after distillation was collected and sealed off in

vacuum in special thin bottomed ampules, these latter being placed in the holder previously mentioned.

After assembly electron tube, vacuum line and manometers were baked with electric furnace and hand torch at 400°C for three hours in a vacuum of 10^{-4} mm or better. At the end of this time the electron tube was heated to glowing with an induction furnace and torching of the line repeated. Finally the filament was heated, the temperature gradually raised to 2600°K and held there for two hours keeping the pressure $<10^{-5}$ mm and a final heating with torch and induction furnace carried out. After completing this process the pressure would in twenty-four hours rise from $<10^{-6}$ mm to $<10^{-5}$ mm with the pump shut off or it would rise a like amount in thirty minutes with the pump shut off and the filament at 2200°K. Such conditions were satisfactory for the present purpose since these pressures of residual gases were responsible for a quantity of negative ions too small to be experimentally detected.

Before each run the filament was aged as recommended by Langmuir and Jones[10] by heating in the water-cooled tube to 2600°K for an hour with continued pumping. After this time the temperature was lowered to running value and held there until the electron emission, as calculated from the observed plate current, had reached a constant value which was approximately equal to the theoretical. The system was then in condition for measurements.

The measurements made consisted in the observation of the plate current as a function of the solenoid current under various conditions of filament temperature and gas pressure. In each set of measurements the temperature of the exposed section of filament was determined from the filament voltage and current by means of the tables of Langmuir and Jones,[10] correction being made for the cooling effect of the leads. The grid and plate potentials were adjusted on the voltmeter and pressures read on either the McLeod gauge or the fiber manometers.

The first two sets of observations were in the nature of controls and were carried out in

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[10] Langmuir and Jones, Gen. Elec. Rev. **419**, 310 (1927); Table I, function No. 6.

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vacuum and in mercury vapor, respectively, the purpose of the first being to determine the efficiency of the solenoid in cutting out the electron current and that of the second to determine the extent of decrease of this efficiency caused by scattering during collisions of electrons and heavy atoms of negligible electron affinity. From the nature of these measurements the conditions under which they were performed (see Table I) were purposely so chosen as to be very unfavorable to electron current extinction compared with those later used for iodine. The first set was conducted in a good vacuum (10^{-6} mm or better) with the pumps running and mercury vapor frozen out; the second set in an atmosphere of mercury (1.84×10^{-3} mm pressure) built up by warming the traps to room temperature.

At the end of these two runs the same determinations were carried out in known pressures of iodine vapor at various filament temperatures. The system was freed from mercury vapor by freezing the line traps with liquid air, the pumps shut off by a mercury seal, the magnetic valve closed and iodine admitted by breaking one of the ampules. The iodine was distilled into the small trap previously mentioned, the temperature of which was maintained at some fixed value in the range from $-40°C$ to $-10°C$ by a cooling alcohol bath contained in a stoppered Dewar. The value of the iodine pressure, which was determined by the bath temperature, was measured on the manometers with the filament at running temperature and the tube walls water-cooled. (Further discussion regarding the pressure measurements is given below.) When the pressure, as measured, had reached a constant value observations of the plate current were carried out. On their completion the iodine was frozen out of the tube by cooling the source with liquid air, the magnetic valve opened and the pressure of non-condensable gases read on the McLeod gauge. This procedure was repeated for various iodine pressures and filament temperatures, with intervals of pumping.

CALCULATIONS AND RESULTS

Combining Eqs. (4) and (5) and solving for $-\Delta E_0$, the electron affinity, one obtains

$$-\Delta E_0 = RT_s \ln \left[\frac{i_{x^-}}{i_{e^-}} \frac{1}{P_{x_2}} \left(\frac{T_G m_{x^-}}{T_s 2 m_{e^-}} \right)^{\frac{1}{2}} \right] + \int_0^{T_s} \Delta C_P dT - T_s \Delta S. \quad (6)$$

For bromine the difference between the atomic ground level, a $^2P_{3/2}$ level, and the next level $^2P_{1/2}$ is 0.45 volt. The value of $e^{-\epsilon/RT}$ at 2000°K is seen to be 0.074, and hence one may neglect the contribution to either specific heat or entropy due to internal excitation. For iodine the energy difference between these two levels is greater. The ions presumably have no excited state lower than 1 volt. The lowest level for all the halogen atoms, a $^2P_{3/2}$ level, has a weight 4, that for the ions, a $^1S_0$ level, a weight 1, whereas the electron has a weight 2.

One may then write for the reaction 1, under consideration, that

$$\int_0^{T_s} \Delta C_P dT = (5/2) RT_s$$

the difference in entropy between atom X and ion X^- is $R \ln 4$, and the entropy of the electron gas, at hypothetical 1 atmosphere pressure, is given by the Stern-Tetrode expression

$$S_{e^-}° = R \ln \left[k(2\pi m_{e^-} kT_s)^{3/2} h^{-2} \cdot 2 T_s e^{5/2} \right].$$

Making the numerical evaluations and introducing logarithms to the base 10 one obtains for $-\Delta E_0$

$$-\Delta E_0 = (4.575/1000) T_s [\log \Delta_{I^-}/\Delta_{e^-} - \log P_{I_2} + 2 \log T_s + 4.073] \text{kcal. for } I. \quad (7)$$

Besides P_{x_2} and T_s the ratio of the galvanometer deflections $\Delta_{I^-}/\Delta_{e^-}$ due to ion and electron current only enters this equation.

In Fig. 3 is shown a typical example of how the electron current to the plate falls off with increasing solenoid current. The plate current, expressed as the fraction of that existing in the absence of the magnetic field, is plotted on a logarithmic scale against the reciprocal of the solenoid current. The curve marked vacuum is for residual gas pressures lower than 10^{-6} mm Hg, the curve marked Hg was observed with 1.8×10^{-3} mm of mercury vapor present in the
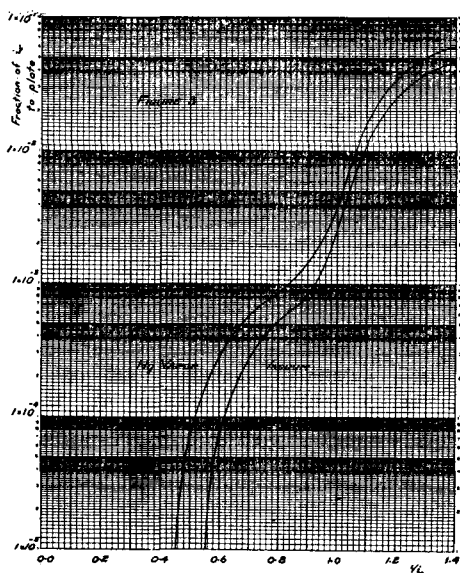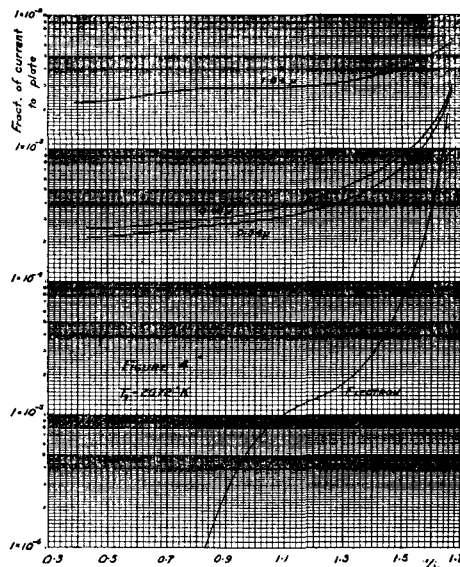
FIG. 3.

FIG. 4.

tube. The grid potential (compared to filament zero), was 20.0 volts, and the plate potential 30.0 volts. The filament temperature was 2100°K. Even under these comparatively unfavorable conditions of high potentials, high filament temperatures, and high residual gas (Hg) pressure the electron current could be eliminated satisfactorily.

Fig. 4 shows the same type of plot for a set of typical experiments with iodine. In this case the grid and plate potentials were 9.0 and 10.0 volts, respectively, and the filament temperature 2072°K. The curve marked "electron" shows the behavior of the plate current under these conditions in the absence of iodine vapor; the three other curves were obtained with 0.34, 0.48 and 1.84 microns (1 micron $= 10^{-3}$ mm Hg) of iodine vapor pressure, respectively. Extrapolation to $1/i_s = 0$ (infinite solenoid current), which can be readily made, gives, directly the desired ratio, $\Delta_{I^-}/\Delta_{e^-}$ to an apparent accuracy of within 20 percent.

The filament temperatures used were about 2000°K and the factor $4.575T/1000$ in Eq. (7) has the numerical value 9.2 kcal. at this temperature. An error of 20 percent in $\Delta_{I^-}/\Delta_{e^-}$

introduces an error of about 0.7 kcal. in the final result, as would a 20 percent error in the measurement of P_{x_2}. Errors in the measurement of T_s, the filament temperature enter in such a way that a 20° or 1 percent error in the temperature introduces a 1 percent or 0.7 kcal. error in the electron affinity. It would appear that the errors introduced from these three causes could not exceed 2 kcal. and most probably are considerably less, since there is no apparent reason why the pressure measurements should not have been good to 10 percent and the temperatures to within $\frac{1}{2}$ percent.

The pressure of iodine in the apparatus, as measured by the quartz fiber manometers, did not, until a considerable time had elapsed, build up to the saturation value corresponding to the temperature of the cooling bath. This interval was sometimes almost an hour after placing the bath on the previously liquid-air cooled iodine. Furthermore, on heating the filament a considerable and permanent drop in pressure due, presumably, to "clean up" effects was observed. For these reasons considerable care was taken in order to be certain that the measured pressures represented accurately the pressure existing in

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the tube. As before mentioned, two quartz fiber manometers connecting directly to the tube were used; the discrepancy between the readings of the two never exceeded 10 percent.

Finally it must be emphasized that, in what seems to us the unlikely case, that the fundamental assumption of nearly zero reflection coefficient for all atom species be in error, an indeterminate error may be introduced in the values of the electron affinity presented, and particularly if there actually be a reflection coefficient of $\frac{1}{2}$ for electrons the results here published must be raised by 2.7 kcal.

TABLE I.

No.	T (°K)	P ($\times 10^3$)	Δ_I^- (cm)	Δ_s^- (cm)	Δ_I^-/Δ_s^- ($\times 10^4$)	$-\Delta E_0$ (kcal.)
1	1942	1.80	2.05	245	83.6	73.9
2	1949	1.55	1.93	243	79.3	74.5
3	1971	0.25	0.87	2050	4.24	71.1
4	2072	0.13	5.87	55300	1.07	72.2
5	2072	0.34	2.65	12500	2.12	71.1
6	2072	0.48	2.15	8300	2.61	70.5
7	2072	1.84	17.30	8550	20.3	73.4
					Ave.	72.4

In Table I the data and calculated electron affinities of the various experiments on iodine are presented.

The method of calculation here employed differs from that previously used in the similar case in which the ionization of caesium atoms to positive Cs^+ ions is observed. The essential difference is that here the work function of the metal does not occur explicitly in the calculation, but instead, the electron emission under the conditions of the experiment is directly observed. No additional assumption is involved in this method of calculation, indeed the difficulty that the work function of the metal is actually changed by the presence of the iodine atmosphere is eliminated.

It may be of interest to tabulate the difference in electron emission observed during the course of these experiments, as compared to that observed[10] from a clean tungsten surface. To present this one may choose to tabulate the value of the work function φ_{WI} of the iodine coated tungsten filament in the various experiments evaluated under the assumption that the temperature independent constant of the emission equation for such surfaces is the same as that for clean tungsten. That is, the observed electron emission in the various experiments differed from the observed emission of clean tungsten by the factor exp $(\varphi_W - \varphi_{WI})/kT_s$ where φ_W, the work function of tungsten, is 4.48 volts and k is expressed in volts. Table II presents these values.

TABLE II. *Work function of tungsten* $(\varphi_W) = 4.48$ *volts.*

T_s (°K)	1942	1949	1971	2072	2072	2072	2072
P_{I_2} ($\times 10^3$)	1.80	1.55	0.25	0.13	0.34	0.48	1.84
φ_{WI} (volts)	5.45	5.46	5.27	5.06	5.33	5.40	5.40

Although no great significance attaches to these values, and it is even conceivable that the whole effect is due to the presence of small oxygen traces, still the results are qualitatively as expected. The work function increases with increasing iodine pressure and attains a constant value at pressures of the order of magnitude of 1 micron.

The final results indicate that the electron affinity of iodine is 72.4 kcal. with a probable error of ± 1.5 kcal.

The authors wish to express their indebtedness to Mr. Harry John, glassblower of the laboratory, for his assistance and advice in the construction of the apparatus.