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## The Electron Affinity of Bromine and a Study of Its Decomposition on Hot Tungsten* **

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The electron affinity of bromine has been measured by determining the ratio of ions to electrons leaving a hot tungsten surface in contact with bromine gas at low pressure. The value obtained is $80.5\pm0.4$ kcal./mole. The measurements, which extend over a range of 700° in temperature and 80-fold in pressure, show no trend in the electron affinity and demonstrate that the decomposition of bromine under these conditions is a first-order reaction. The assumption of unit accommodation coefficient is shown to be correct.

## INTRODUCTION

THE electron affinity is defined as the energy change $(-\Delta E_0)$ accompanying the union of an electron and an atom at absolute zero. Thus the electron affinity corresponds precisely to the ionization potential of its univalent negative ion. In contrast to the complete tables of ionization potential (electron detachment) of atoms there exists only a small number of less accurately determined electron affinities (electron attachment). The small number of values reflects the small number of stable negative monoatomic ions, while the lack of accuracy indicates the absence of spectroscopic measurements. The general agreement that the capture of electrons by atoms with the simultaneous emission of radiation is an improbable event accounts for the failure of spectroscopists to measure directly electron affinities. Indirect spectroscopic measurements are uncertain.

This investigation is concerned with the direct measurement of the electron affinity of bromine by a refinement of the method of Sutton and Mayer,[1] which permits increased precision and an extension of the measurements to larger ranges of temperature and pressure.

### PRINCIPLE OF THE METHOD

By a suitable experimental arrangement (see Apparatus) it is possible to measure the ratio of bromine ions to electrons leaving the surface of a hot tungsten wire surrounded by bromine at a constant pressure. This ratio, together with the pressure of bromine and the temperature of the wire, is sufficient to calculate the equilibrium constant and hence the energy change (the electron affinity) of the reaction

$$Br + e \rightarrow Br^-. \tag{1}$$

The assumption must be made in such a calculation that all the bromine molecules which hit the hot filament come to thermal equilibrium with the filament and dissociate and ionize accordingly. Then it follows that the number of

[1] P. P. Sutton and J. E. Mayer, J. Chem. Phys. **3**, 20 (1935).
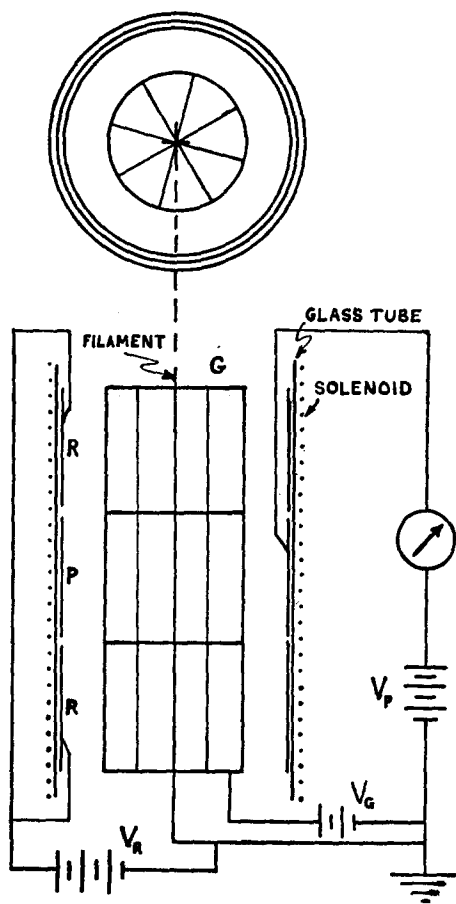
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FIG. 1.

bromine atoms leaving the filament is related to the pressure $P_{Br}$ of bromine atoms in a gas at the same temperature as, and in equilibrium with, the surface by

$$Z_{Br} = \frac{P_{Br}}{(2\pi m_{Br} k T_s)^{\frac{1}{2}}}, \quad (2)$$

where $T_s$ is the temperature of the surface. If the temperature of this surface corresponds to virtually complete dissociation of bromine (greater than 1500°C) at existing pressures and if a negligible fraction of the atoms are converted into ions (which is true in this case), then one may equate the number of molecules hitting to half the number of atoms leaving the surface. This yields the expression

$$P_{Br} = P_{Br_2}(4m_{Br}T_s/m_{Br_2}T_r)^{\frac{1}{2}} = \sqrt{2}P_{Br_2}(T_s/T_r)^{\frac{1}{2}}, \quad (3)$$

where $P_{Br_2}$ is the pressure of $Br_2$ surrounding the filament at temperature. The ion-electron ratio

can be used as follows to obtain an expression for the pressure ratio

$$P_{Br-}/P_e = (i_{Br-}/i_e)(m_{Br}/m_e)^{\frac{1}{2}} \quad (4)$$

of ions and electrons in the hypothetical equilibrium gas.

Combining (3) and (4) the equilibrium constant and the standard free energy change of the reaction (1) may be written as

$$K = \exp\ (-\Delta F^0/RT_s) = P_{Br-}/P_e P_{Br}$$
$$= (1/\sqrt{2})(i_{Br-}/i_e)(1/P_{Br_2})(m_{Br_2}T_r/m_e T_s)^{\frac{1}{2}}. \quad (5)$$

The standard free energy change is related to the electron affinity $(-\Delta E_0)$ by the equation

$$-\Delta E_0 = -\Delta F^0(T)$$
$$+ F^0_{Br-}(T) - F^0_e(T) - F^0_{Br}(T). \quad (6)$$

Since the free energy of each of the species is given by

$$F^0(T) = RT \ln\ (h^2/2\pi m k T_s)^{\frac{3}{2}}(1/kT_s Q') \quad (7)$$

at unit pressure, Eq. (6) may be written as

$$-\Delta E_0 = RT_s \ln\ [(\sqrt{2}\pi^{3/2}k^{5/2}/h^3)m_e(m_{Br_2})^{\frac{1}{2}}$$
$$\times (i_{Br_2}/i_e)(T_s^2 T_r^{\frac{1}{2}}/P_{Br_2})(Q'_{Br}Q_e'/Q'_{Br})]. \quad (8)$$

The internal partition function $Q'$ for electrons is 2. It is believed that no states of the bromide ion exist above the ground state, inasmuch as the nuclear shielding becomes practically complete when the electron is in a quantum state higher than the ground state. Consequently $Q'_{Br-}$ is set equal to one since the ground state is a singlet. The lowest term of the bromine atom $^2P_{3/2}$ has a degeneracy of 4 while the next member of the doublet lies 3685 cm$^{-1}$ above the ground state. Thus we have

$$Q'_{Br} = 4 + 2e^{-5300/T}. \quad (9)$$

The second term contributes, at the most, 0.05 kcal./mole to the electron affinity and hence this will be neglected.

Evaluating the constants in Eq. (8) one obtains for the working equation with $\Delta E_0$ in kilocalories per mole and $P_{Br_2}$ expressed in microns,

$$-\Delta E_0 = 4.575\frac{T_s}{1000}\left(\log\ 100\frac{i_{Br-}}{i_e} - \log\ P_{Br_2}\right.$$
$$\left. + 2\log\frac{T_s}{1000} + 7.964\right). \quad (10)$$

## DESCRIPTION OF APPARATUS

The central part of the apparatus, the reaction tube, was constructed along lines similar to that described previously.[2] This is shown schematically in Fig. 1. The filament $F$ is suspended vertically by means of a tungsten spring so that it is kept taut when heated electrically. This is closely surrounded by a radial grid $G$ and the latter by cylindrical plates and guard rings $P$ and $R$. These are fixed in a Pyrex tube, and the whole surrounded on the outside by the solenoid $S$, coaxial with $F$. By means of a suitable electrical system, $G$ and $P$ and $R$ may be maintained at the potentials $V_G$ and $V_P$, respectively, with $V_P$, $V_G$, $V_F$. The flow of current to the plate may then be determined by means of the galvanometer connected in series with $P$.

When the tube is filled with the bromine, streaming through at constant pressure, and the filament heated to a known temperature, ions and electrons will travel radially to the plate, giving a galvanometer deflection. If a current is passed through the solenoid, the electrons will be deflected into the grid, while there will be no appreciable effect on the current to the plate due to the heavy ions. Therefore the galvanometer deflections due to ions $i_i$ and to electrons $i_e$ may be determined independently under fixed conditions of $P_{Br_2}$ and $T_s$.

The reaction tube used here differed from the



FIG. 2.

one described[2] in that a large ground glass joint (lubricated with graphite and Apiezon L) replaced the glass seal in joining the filament and

grid support to the reaction tube. Furthermore, a longer filament (11.34 cm) was used and this was soldered directly to the supports.

A control tube, similar to the reaction tube but without grid, plate, and guard rings, was mounted in series with the reaction tube. This control tube was not necessary for the actual measurements but was used for the measurement of heat loss of the wire described later.

The diagram (Fig. 2) of the vacuum system shows how bromine is permitted to leak through the capillary $C$ at a rate determined by the temperature of the trap $T$. After flowing through the tubes it is frozen out in trap $T'$ which is cooled in liquid nitrogen. At the end of the run the bromine is removed by distilling into the bulb $B$ which can be detached and emptied without breaking the vacuum in the system.

The pressure is measured with a quartz fiber gauge. The decay of the fiber oscillations is observed by light reflected into a telescope with a graduated eyepiece. The gauge is surrounded by mineral oil to prevent external vibrations from reaching the fiber.

In order to make measurements at lower filament temperatures a FP-54 amplifier was constructed and the input connected to the plate of the reaction tube. This enabled one to measure plate current with a sensitivity of $1 \times 10^{-14}$ amp./mm.

## THE ATTAINMENT OF THERMAL EQUILIBRIUM ON THE SURFACE

The assumption of unit accommodation coefficient which is necessary for the above derivation is supported by a large amount of evidence of an indirect nature.[2, 3] Three additional points are offered below which indicate the correctness of this assumption.

(1) It has been shown recently[4] by calculations based on the data of Bryce[5] that the assumption is true for the case of hydrogen molecules and hot tungsten; i.e., all the hydrogen molecules hitting a hot tungsten filament come to equilibrium concentrations determined by the temperature of the filament and the number of molecules striking. It is quite reasonable then that the
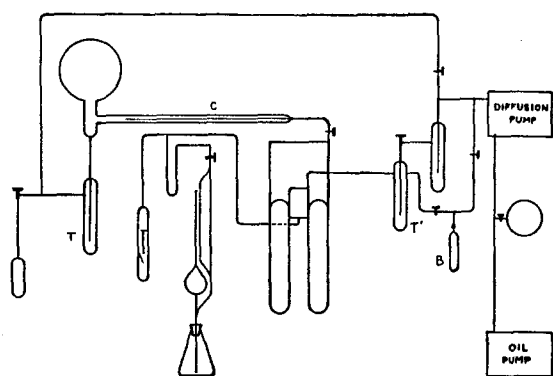
[2] K. J. McCallum and J. E. Mayer, J. Chem. Phys. 11, 55 (1943).

[3] H. B. Weisblatt, Dissertation, Johns Hopkins University, 1938.
[4] P. M. Doty, J. Chem. Phys. 11, 557 (1943).
[5] G. Bryce, Proc. Camb. Phil. Soc. 32, 648 (1936).

same situation may exist for the halogens and tungsten.

(2) In this investigation measurements of the electron affinity have been made over a range of 80-fold in pressure and 700° in temperature. No change or trend in the calculated value of the electron affinity could be detected. Since a change of accommodation coefficient is equivalent to a corresponding change in pressure, our data show that over the ranges covered by the experiment the accommodation coefficient could not have changed more than 10 percent. It seems reasonable to explain a constant accommodation coefficient by a value of unity.

(3) If all the bromine molecules which collide with the hot filament decompose, the filament should lose energy by an amount equal to the heat of dissociation of the molecules hitting plus the energy given to the atoms formed. Now the energy loss to the filament may be found by measurements of the current passing through the filament and the voltage across the filament, first for a vacuum and then for a given pressure of bromine. From these one may calculate the watts $w$ used and the resistance $R$ of the filament. Using this information one may then determine the energy loss $D$ of the filament due to the bromine by means of the equation:

$$D = (W_{vac} - W_{Br_2}) - [(dW/dT)/(dR/dT)]$$
$$\times (R_{vac} - R_{Br_2}). \quad (11)$$

This has been done at a pressure of 21 microns at various temperatures. In Table I are recorded the temperatures (from the resistance function) together with the observed energy loss per mole of bromine and the theoretical energy loss (calculated on the basis of a unit accommodation coefficient) which is the energy $E$ of dissociation at room temperature $T_r$, plus $3R(T_f - T_r)$ for the energy given to the two moles of bromine atoms formed. This table shows that the energy loss of the filament corresponds within experimental error ($\sim$15 percent) to the energy loss that would occur if the accommodation coefficient were unity. The energy loss differs from that calculated in the direction that is impossible according to the laws of thermodynamics. We may say that these experiments show the existence of unit accommodation coefficient. Similar

TABLE I. Energy loss of tungsten filament surrounded by bromine.

| Temp. (Vac.) °K | Temp. (Bromine) °K | Observed energy loss kcal./mole | $E + 3R(T_f - T_r)$ kcal./mole |
|---|---|---|---|
| 2021 | 1987 | 62 | 55.5 |
| 1798 | 1753 | 62 | 54.5 |
| 1622 | 1560 | 54 | 52.1 |

calculations on data obtained during the measurements yield results which are similar but less accurate because at the lower pressures the effect was smaller. The objection may be raised that the presence of some bromine on the surface may increase the emissivity of the filament. However, this effect is not likely to be appreciable inasmuch as the heat loss measurements show no trend and since the amount of bromine present at any instant is probably much less than a monoatomic layer.

## MEASUREMENTS

The values of the electron affinity calculated from the measurements in this investigation show a dispersion which is less than that of other investigations[1,2] by at least a factor of two. It is believed that this increased precision is largely due to the use of an improved technique of obtaining filament temperatures.

The filaments were aged by suspending a loop of tungsten wire (25 cm), held taut by a weight, in a vacuum. After being heated to 2800°K for 15 minutes two straight pieces were cut from the loop. The diameter was determined to 0.01 percent by weighing and measuring the lengths with a cathetometer. These filaments were mounted in the control and reaction tubes which were then baked out in a vacuum overnight (450°C).

Measurements of current and voltage were made immediately after passing sufficient current through the two filaments in series to bring them to a moderate temperature (about 2000°K). It was observed that the resistance and wattage agreed accurately with those of a filament of the known diameter tabulated by Jones and Langmuir.[6]

During the runs the diameter alters with time, but by measuring watts *versus* resistance in vacuum several times during the run the diam-

[6] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **419**, 310 (1927).

eter may be determined accurately for that run. That the procedure was correct could be checked by observing that with this calculated diameter the temperatures obtained from the watts, and from the resistances agreed to within two degrees at all temperatures. The resistance function was used to obtain the temperature when bromine was present.

The bromine (Mallinckrodt N.F.) was distilled several times in vacuum, the first portion of the distillate being discarded each time. This was done in order to eliminate chlorine and fluorine, the only impurities that would introduce an error greater than their effect on the pressure determination. The maximum amount of chlorine present in the undistilled bromine was 0.3 percent. Assuming all this remained after distillation the electron affinity here obtained would be 0.04 kcal. too large.

The silver parts of the reaction tube (grid, plate, and guard rings) were coated with silver chloride to prevent reaction with bromine.

In a typical run the grid potential would be set at 3 volts and the plate and guard rings at 6 volts positive with respect to the positive and of the filament, i.e., the end which is not grounded. After voltage and current measurements were made in a vacuum, bromine was allowed to flow through the system at a constant rate. Voltage and current measurements were repeated with the filament at a steady temperature and the

TABLE II. Electron affinity of bromine.

| Pressure (microns) | Temp. °K | $100(i_{Br^-}/i_e)$ | $-\Delta E_0$ | Deviation |
|---|---|---|---|---|
| 21.2 | 1966 | 53.9 | 80.62 | +0.13 |
| 17.2 | 2180 | 4.25 | 80.21 | −0.28 |
| 9.50 | 2276 | 0.883 | 79.87 | −0.62 |
| 6.90 | 1929 | 25.6 | 80.35 | −0.14 |
| 6.80 | 1878 | 52.8 | 80.78 | +0.29 |
| 5.40 | 2048 | 5.13 | 80.26 | −0.23 |
| 4.85 | 2110 | 2.24 | 79.90 | −0.59 |
| 3.50 | 1893 | 20.6 | 80.45 | −0.04 |
| 2.60 | 1943 | 8.1 | 80.29 | −0.20 |
| 2.00 | 2034 | 2.36 | 80.51 | +0.02 |
| 1.85 | 2217 | 0.377 | 80.92 | +0.43 |
| 1.74 | 2106 | 1.09 | 80.98 | +0.49 |
| 1.72 | 2143 | 0.775 | 81.11 | +0.62 |
| 5.00 | 1823 | 91.0 | 81.02 | +0.53 |
| 1.43 | 1678 | 118. | 79.99 | −0.50 |
| 1.10 | 1679 | 125. | 80.44 | −0.05 |
| 0.88 | 1607 | 263. | 79.78 | −0.71 |
| 0.39 | 1610 | 172. | 81.29 | +0.60 |
| | | Average | 80.49 | 0.36 |

TABLE III.

| Investigator | Reference | Value kcal./mole | Method |
|---|---|---|---|
| Ionov | a | 83.9 | Ratio of + to − ions on hot tunsten hit by beam of KBr |
| Weisblatt, Mayer | b | 80.0 | Similar to this but with less accuracy Only two temperatures |
| Van Arkel, de Boer | c | 87.6 | Born cycles |
| Mayer and Helmholtz | d | 81.5 | Born cycles |
| Verwey and de Boer | e | 77.2 | Born cycles |
| Huggins, Rice | f | 81.8 | Born cycles |
| Glockler, Calvin | g | 88. | Experimental (space charge) |
| Mayer and Helhmoltz | h | 88.3 | Dissociation of alkali halides |
| Saha and Tandon | i | 80.0 | Dissociation of alkali halides |
| Blewett | j | 87. | Mass spectrograph |
| Lederle | k | 82. | Absorption spectra |
| This experiment | | 80.5±0.4 | |

a N. I. Ionov, Comptes rendus Acad. Sci. U.S.S.R. 28, 512 (1940).
b See reference 3.
c A. E. Van Arkel and J. H. De Boer, Physica 7, 12 (1927).
d J. E. Mayer and L. Helmholtz, Zeits. f. Physik 75, 19 (1932).
e E. J. W. Verwey and J. H. De Boer, Rec. trav. chim. 55, 431 (1936).
f M. L. Huggins, J. Chem. Phys. 5, 143 (1937).
g G. Glockler and M. E. Calvin, J. Chem. Phys. 3, 771 (1935).
h L. Helmholtz and J. E. Mayer, J. Chem. Phys. 2, 245 (1934).
i N. K. Saha and A. N. Tandon, Proc. Nat. Inst. Sci. Ind. 3, 387 (1937).
j J. P. Blewett, Phys. Rev. 49, 900 (1936).
k E. Lederle, Zeits. f. Physik 7, 328 (1933).

pressure and galvanometer deflections (with and without solenoid current on) were recorded. Frequently the effect of solenoid current would be checked and any value between 3 and 6 amperes was found to be satisfactory. For each calculation of electron affinity several measurements of pressure, filament current and voltage, and plate current were made. When the amplifier was used (below 1850°K) the measurements of plate current with and without solenoid were made using the same grid leak in the amplifier in order to avoid errors that might arise from the relative calibration of two leaks.

## RESULTS

In Table II are listed the results of this investigation. The pressure, temperature, and ratio of ions to electrons are given together with the electron affinity calculated from Eq. (10) and the deviations from the mean. Every measure-

ment made after the preliminary work was finished is included in Table II. These measurements extend from 1607° to 2276°K and from 0.39 to 21.2 microns pressure of bromine. The measurements could have been extended somewhat beyond this range, but with increasing difficulty. At higher temperatures (when the electron current exceeds $10^{-3}$) the plate current becomes space charge controlled. At temperatures lower than 1600° pressures too low for accurate measurement on the quartz fiber gauge are necessary. The last five measurements in Table II were obtained with the aid of the amplifier.

The assignment of a precision measure to the value of the electron affinity is found by taking the square root of the sum of the squares of the deviation of the mean and the residual errors. The deviation of the mean (A.D.) is ±0.08. The residual error in the temperature measurements is estimated to be 5° (0.25 percent), in the pressure 8 percent, in the ion-electron ratio 5 percent; these correspond respectively to errors of 0.2, 0.3, and 0.2 kcal./mole in the calculated electron affinity. In this manner one arrives at a precision measure of ±0.42. Thus, the electron affinity of bromine is found to be 80.5±0.4 kcal./mole.

Several other investigations of the electron affinity of bromine are summarized in Table III.

## DISCUSSION

Another observation may be made from the constancy of the calculated values of the electron affinity presented in Table II. This constancy shows the correctness of the assumption made at the beginning requiring the pressure of bromine atoms leaving the surface to equal twice the pressure of bromine molecules in the gas phase. This corresponds precisely to the definition of a first-order reaction. Hence the decomposition of bromine on tungsten above 1600°K and below 22 microns pressure is a first-order reaction with an activation energy equal to the energy of decomposition. This may be compared with the first-order decomposition of hydrogen iodide on platinum[7] and of nitrous oxide on gold.[8] On the other hand, the high temperature decompositions of ammonia on tungsten[9] and hydrogen iodide on gold[10] are zero-order reactions.

[7] C. N. Hinshelwood and R. E. Burk, J. Chem. Soc. 127, 2896 (1925).
[8] C. N. Hinshelwood and C. R. Prichard, Proc. Roy. Soc. A108, 211 (1929).
[9] C. H. Kunsman, E. S. Lamar, and W. E. Deming, Phil. Mag. 10, 1015 (1930).
[10] C. N. Hinshelwood and C. R. Prichard, J. Chem. Soc. 127, 1552 (1925).