Ionization Processes on Tungsten Filaments I. The Electron Affinity of the Oxygen Atom

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a statistical mechanical interpretation as the average values of appropriate microscopic quanties of molecular character, it can be hoped that a similar interpretation will be possible in the case of microscopic portions of a system. Thus, it might be natural to begin by taking the quantity γ, at any point x in the transition layer, as the time average of the density of fluid at that point, and then proceed by assigning to p and ψ the values of pressure and of free energy per gram which would be exhibited by fluid in bulk at the density γ and at the temperature of interest. The interpretation of ϕ presents more difficulty, since it involves some kind of successful distinction between very short-range molecular forces which depend on the immediate local condition of the fluid and only slightly longer range molecular forces which depend on the change in condition with position. It would seem reasonable, however, to expect that ϕ could be interpreted as an appropriate average of that part of the energy per gram at any

point, which depends on the derivatives of γ with respect to x.

With regard to the validity of (16.1), it seems rational for the present to extend the application of this macroscopically verified equation to microscopic regions, and for the future to expect that such an extension will find added statistical mechanical support, substituting appropriate averages of the kind suggested above into the equation. In addition, we may again call attention to the successful use of the consequences of (16.1) to derive, at least for a special case, significant results which can also be derived by the method of Gibbs. This outcome can, of course, not be taken as a sufficient criterion for the validity of (16.1) but can nevertheless increase our confidence therein.

For the time being, it would seem a sensible procedure to make tentative use of the consequences of our detailed treatment when we need them to supplement the consequences of the less detailed treatment of Gibbs.

Ionization Processes on Tungsten Filaments

I. The Electron Affinity of the Oxygen Atom*

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The electron affinity of the oxygen atom was determined to be 53.8 ± 0.8 kcal./mole by measuring the ratio of ions to electrons leaving a hot tungsten filament in contact with nitrous oxide gas at a low pressure. Previous investigations of this quantity yielded discordant results. A possible reason for this disagreement is set forth.

INTRODUCTION

DIRECT experimental determinations of the electron affinity of the oxygen atom have

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been made by Vier and Mayer,[1] Lozier,[2] and Hanson.[3] These workers obtained, respectively, values of 70.8 ± 2, 51 ± 5, and 46 ± 9 kcal./mole. This investigation was undertaken in an attempt to resolve these differences. The method used,

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[1] D. T. Vier and J. E. Mayer, J. Chem. Phys. **12**, 28 (1944).
[2] W. Lozier, Phys. Rev. **46**, 268 (1934).
[3] G. Hanson, Phys. Rev. **48**, 476 (1935).

that of Vier and Mayer, has been successful in determinations of the electron affinities of the atoms of chlorine,[4,5] bromine,[6] and iodine.[7] In this method, molecules containing the atom, X, whose electron affinity we wish to measure, are allowed to dissociate on the surface of a hot tungsten filament:

$$AX_n \rightarrow nX + A. \qquad (1)$$

The resulting X atoms react with the electrons emitted from the filament according to the reaction

$$X + e^- \rightarrow X^-. \qquad (2)$$

The negative of the energy change of this reaction at 0°K, $-\Delta E_0$, is the electron affinity of X. From measurements of the relative electron and ion currents from the filament, the equilibrium constant of this reaction, and hence the electron affinity, can be calculated.

One of the requirements for the success of the method is an accurate knowledge of the rate of formation of X atoms at the filament. Vier and Mayer[1] used oxygen molecules as their source of oxygen atoms. The dissociation of these molecules is far from complete, and difficulty arises in the computation of the extent of the dissociation. In addition, the possibility of the formation of O_2^- cannot be disregarded. Other carriers, such as CO, CO_2, and SO_2, have the disadvantage of possibly changing the filament characteristics. Others, such as NO, are not completely dissociated at filament temperatures. In order to avoid these difficulties, we have used nitrous oxide as the carrier gas. We believe that N_2O dissociates completely into N_2 and O at the filament temperatures used, 2000°K to 2400°K, since dissociation is substantially complete at 1200°K.[8]

THEORY

It has been shown by McCallum and Mayer[4] that if a gas at temperature T_r and pressure P_r,

[4] K. J. McCallum and J. E. Mayer, J. Chem. Phys. 11, 56 (1943).

[5] J. J. Mitchell and J. E. Mayer, J. Chem. Phys. 8, 282 (1940).

[6] P. M. Doty and J. E. Mayer, J. Chem. Phys. 12, 323 (1944).

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

[8] L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, New York, New York, 1932).

TABLE I. Electron affinity of the oxygen atom with N_2O as carrier.

Run	T, °K	P, μ	$i_i/i_e \times 10^5$	$-\Delta E_0$
I	2192	3.1	3.7	53.2
	2186		3.2	52.5
	2210		3.0	52.7
	2260		1.0	49.3
II	2131	12.2	30	54.6
	2134		16	52.0
	2202		16	54.0
	2305	11.4	7	53.4
	2292		8.9	54.1
	2289		14	56.1
	2342		9.3	55.8
	2342		4.4	52.3
III	2177	11.9	24	55.1
	2273		10	54.0
	2213		19	55.1
	2213		15	54.1
	2106		55	56.5
IV	2268	11	9.5	54.4
	2266		5.7	51.3
	2136		27	55.2
	2163		21	54.2
	2181	8.4	17.5	55.3
	2177		22	56.3
	2138	7.7	25	55.0
	2168		16	55.0
	2278		3.6	51.6
	2278		6.2	54.1
V	2092	6.6	16	53.4
	2111	4.6	11	53.9
	2202		5.3	53.3
	2202		5.9	53.8
	2276		3	52.9
	2279		1.8	50.6
	2082		17	54.8

53.8 av.
a.d. = 1.3
P. E. = 0.2

composed of molecules of mass m_r containing n atoms X whose electron affinity is to be measured, is completely decomposed at a filament at the temperature T_s and gives an ion current i_i and an electron current i_e, then the electron affinity, $-\Delta E_0$, is given by

$$-\Delta E_0 = RT_s \ln\left[\frac{2^{5/2}\pi^{3/2}k^{5/2}}{h^3} \frac{m_e m_r^{1/2}}{n} \times \frac{i_i}{i_e} \frac{T_r^{1/2}T_s^2}{P_r} \frac{Q_x'}{Q_i'}\right] \qquad (3)$$

where m_e is the mass of the electron, Q_x' and Q_i' are the internal partition functions for the atoms X and the ions X^-, and the other symbols have their usual significance. This equation also applies even if the carrier molecules are not com-

TABLE II. Results of the calculation of the electron affinity of the oxygen molecule, calculated on the assumption of the reaction $O_2+e^-\rightarrow O_2^-$, and of the oxygen atom, with oxygen as carrier gas.

T, °K	P, μ	$i_i/i_e \times 10^4$	$-\Delta E_0(0)$	$-\Delta E_0(O_2)$
2052	6.65	80	72.5	66.0
2151	5.3	21	68.5	64.8
2306	4.45	3.0	62.7	61.5
		2.4	61.7	
2386	4.1	1.9	62.4	61.9
		1.2	60.3	
2170	4.8	46.2	73.1	69.2
2207	0.67	6.15	70.3	70.3
2396	0.67	0.31	61.8	62.5
		0.26	61.0	
2282	0.67	2.05	67.4	68.1
				65.5 av.
				a.d. = 2.8

pletely dissociated into atoms, as long as all the atoms X are completely dissociated from the rest of the molecule. Equation (3) can, therefore, be used for the electron affinity of oxygen with N_2O as the carrier, since the N_2O molecule can be assumed to dissociate into N_2 and O.

In the work of Vier and Mayer, in which O_2 was used as the carrier, the assumption of complete dissociation at the filament could not be made. If a fraction β of the carrier is dissociated, Eq. (3) can be corrected for incomplete dissociation by replacing P_r by βP_r. Vier and Mayer calculated β by assuming that temperature equilibrium was reached between the carrier O_2 and the filament. This, however, introduces a possible error into the results.

Vier and Mayer have used the following expressions for Q_x' and Q_i' for oxygen atoms and ions:

$$Q_x' = 5+3\exp(-226.2/T_s)+\exp(-324.5/T_s)$$
$$Q_i' = 6.0. \qquad (4)$$

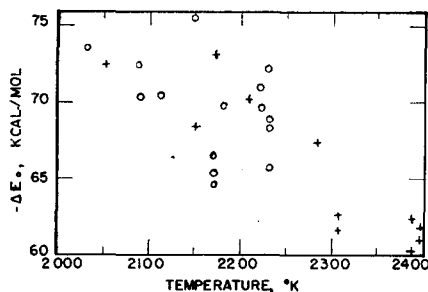
FIG. 1. Electron affinity of O, calculated on the assumption of the reaction $O+e^-\rightarrow O^-$, plotted against filament temperature, for runs with oxygen as carrier gas. This experiment +; Vier and Mayer O.

Using these expressions and evaluating the numerical constants, the electron affinity of oxygen in kcal./mole is

$$-\Delta E_0 = 4.574\times10^{-3}T_s[\log10^4 i_i/i_e - \log P_r$$
$$+2\log10^{-3}T_s - \log n - \log\beta$$
$$+\tfrac{1}{2}\log M + 4.722], \qquad (5)$$

if P_r is expressed in microns, and where M is the molecular weight of the carrier. In deriving this equation, a term $0.09342\times10^{-4}T_s$ has been approximated by the constant value 0.020.

With N_2O as the carrier gas, we have used $n=1$ and $\beta=1$. With O_2 as the carrier, $n=2$ and β has been calculated in the way described by Vier and Mayer.

If we assume the observed ion current to be due to O_2^- ions, formed as a results of the reaction

$$O_2+e^-\rightarrow O_2^-, \qquad (6)$$

we set $n=1$ and $\beta=1$ and assume as a first approximation that $Q_x'=Q_i'$. The numerical constant in Eq. (5) is then 4.568.

EXPERIMENTAL

Previous papers have described the essential features of the apparatus. The Pyrex reaction tube contained a central tungsten filament, of 0.02 cm diameter, a radial nickel grid, and a nickel plate with two guard rings, all approximately co-axial. A water cooled solenoid was placed around the outside of the tube. Since this tube was also used for an investigation of fluorine, the tungsten helix that was used to keep the filament taut was nickel plated, and all other metal parts in the tube were constructed of nickel. All tungsten leads were encased in glass.

The measurements consisted of the determination of ion current, electron current, filament temperature, and pressure. With the plate at a positive potential with respect to the filament, electrons and negative ions are collected on the plate, and the plate current is the sum of the current due to ions and of that due to electrons. This current is measured with a Leeds and Northrup type HS galvanometer with a sensitivity of 2.3×10^{-10} amp./mm. On passing a current through the solenoid, a magnetic field with B approximately 0.03 weber/m² (300 gauss)

is produced parallel to the filament. This field is sufficient to deflect the electrons to the radial grid, while the ions are practically unaffected. The plate current is then equal to the negative ion current, and the electron current can be found by difference. For each value of the filament temperature, several values of the plate voltage were used, ranging in value from 6 to 45 volts positive with respect to the positive end of the filament. The grid was normally kept 3 volts negative with respect to the plate. The effect of changing solenoid current was occasionally checked. Any current of more than four amperes gave satisfactory results, in that the ratio of the plate current with the magnetic field to that without field was less than 10^{-5} in vacuum, and i_i did not change with solenoid current in the presence of gas. Most measurements were taken at about six amperes solenoid current.

The temperature of the filament was determined by means of the R/R_{293} function for tungsten as tabulated by Jones and Langmuir.[9] Since the diameter of the wire changes during the run, the assumption of a linear change of diameter with time was made. The runs were kept to less than thirty minutes so that this assumption produces only a small error in the calculated temperature. The diameter was determined before and after each run as follows. The voltage and current were measured at several temperatures between 1900°–2300°K in vacuum. From these, the temperature was determined by means of the diameter-independent $VA^{\frac{1}{2}}/l$ function given by Jones and Langmuir. From this temperature, and the resistance, R_{293} and the diameter could be calculated. These diameters agreed within 0.5 percent with diameters obtained by weighing and measuring filaments, both before insertion in the reaction tube and after removal from the tube after a series of runs.

Pressure measurements were made by means of a quartz fiber gauge which had been calibrated with dry air against a McLeod gauge. Damping at the fiber was observed by means of a telescope with a graduated eyepiece. The gauge was suspended from the reaction tube by a glass helix and was surrounded by mineral oil to minimize

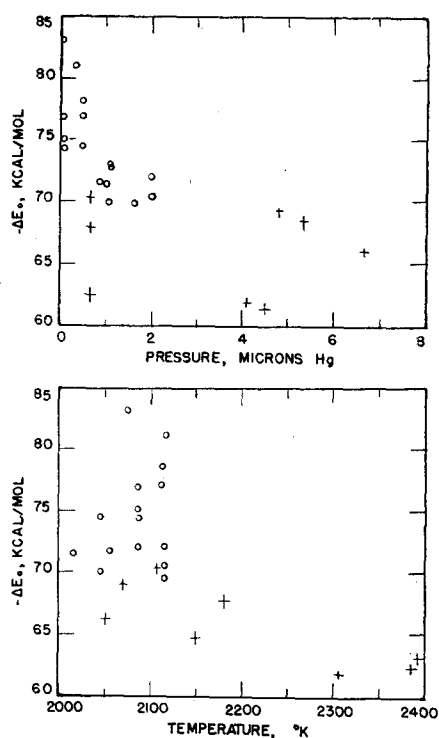[9] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 312 (1927).

FIG. 2. Electron affinity of O_2, calculated on the assumption of the occurrence of the reaction $O_2 + e^- \rightarrow O_2^-$, plotted against filament temperature and against pressure. This experiment +; Vier and Mayer O.

the effect of external vibrations. The calibration was reproducible to within 10 percent.

The nitrous oxide, of 98 percent purity, was obtained from the Matheson Co. It was purified by condensing it into a liquid nitrogen trap and pumping off any non-condensible gases. The nitrous oxide was then distilled off while the trap was kept cold with dry ice-acetone mixture, leaving behind any more condensible impurities. This procedure was repeated three times. The nitrous oxide was then transferred to a two-liter reservoir bulb which was connected to the system by a capillary leak.

The error in the measurement of the filament temperature is less than 10°, on the basis of the reproducibility of measurements made in vacuum and the calculation of the temperature by several different methods. An error of 10° in a single temperature measurement would lead to an error of 0.5 percent or 0.25 kcal./mole in the electron affinity calculated from that measurement. The pressure measurements are in error by less than 10 percent, as calculated from the

behavior of the quartz fiber gauge during calibration. An error of 10 percent in the pressure would result in an error of 0.5 kcal./mole in the electron affinity. The error in the current ratio ranged from 10 percent at high temperatures to as much as 50 percent at low temperatures. This would result in 0.5 to 3 kcal./mole error in $-\Delta E_0$. This leads to a precision measure of ± 0.8 for measurements at temperatures greater than 2100°K.

RESULTS

Table I lists the experimental results and calculated electron affinities of the oxygen atom with nitrous oxide as carrier gas.

Table II lists the results with oxygen as carrier gas. This table includes the calculated electron affinity of O_2, computed on the assumption that reaction (6), $O_2 + e^- \rightarrow O_2^-$, is the dominant source of the observed ions, and it also lists the calculated electron affinity of 0, computed on the assumption that the ions formed are O^-. Figure 1 is a plot of the calculated electron affinity of 0 as a function of temperature. The data of Vier and Mayer are included for comparison. Figure 2 includes plots of the calculated electron affinity of O_2 as a function of pressure and of temperature.

DISCUSSION OF RESULTS

Figure 1 shows that the runs with oxygen give substantially the same results as those of Vier and Mayer but that an extension of the experimental temperature range introduces a decided dependence of the calculated electron affinity on temperature. This indicates that some assumption in the calculation of the electron affinity is not justified and that the calculated electron affinity is presumably not the true electron affinity of the oxygen atom. Figure 2 shows that

there is no dependence of the calculated electron affinity of O_2 on either pressure or temperature. Therefore, it seems possible that the ions observed were actually O_2^-. However, other experimental determinations of the electron affinity of O_2 have resulted in values of 3 kcal./mole[10] and 8 kcal./mole.[11] Although an estimation of this quantity from the heat of dissociation and heat of solution of HO_2 is 62 kcal./mole[12] the values obtained seem to be unreasonably high. The results are not sufficiently clear for a conclusive interpretation to be made.

The results of the runs with N_2O as carrier gas are free of any trend with temperature over a range of 2092–2340°K and with pressure from 4 to 12 microns. The average value of 53.8 ± 0.8 kcal./mole agrees within experimental error with the results of Lozier and of Hanson.

CONCLUSION

1. We have shown that the results of the measurements using oxygen gas as the carrier cannot be interpreted as giving the correct electron affinity of oxygen atom. They may possibly give the electron affinity of oxygen molecule, but this appears to be unlikely.

2. The electron affinity of the oxygen atom is 53.8 ± 0.8 kcal./mole, in agreement with the results of Lozier and of Hanson.

[10] N. E. Bradbury, J. Chem. Phys. 2, 627 (1394); ibid., 2, 835 (1934).
[11] L. B. Loeb, Phys. Rev. 48, 684 (1935).
[12] J. Weiss, Trans. Faraday Soc. 31, 966 (1935).