Ionization Processes on Tungsten Filaments II. The Absorption of Fluorine on Tungsten

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Ionization Processes on Tungsten Filaments

II. The Absorption of Fluorine on Tungsten*

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Fluorine is found to form an adsorbed film on tungsten stable to temperatures above 2600°K. This causes a low accommodation for the thermal dissociation of fluorine. The adsorption is compared to that of oxygen on tungsten.

INTRODUCTION

THIS investigation was begun as an attempt to measure the electron affinity of fluorine by the method described in the preceding paper[1] of passing fluorine gas at a given pressure over a hot tungsten filament and measuring the relative currents of negative ions and electrons emitted from the filament. It soon became evident, however, that the current of negative ions was much smaller than would be expected from any reasonable estimate of the electron affinity of fluorine and that this discrepancy decreased as filament temperature was raised. Further investigation has led to the conclusion that the fluorine gas is not completely dissociated, predictions, based on the equilibrium constant for the dissociation,[2] to the contrary. This paper is an attempt to elucidate this behavior.

The apparatus and techniques used were those described in Part I.

EXPERIMENTAL OBSERVATIONS

The following experimental observations form the basis for the picture given here of the interaction of fluorine and tungsten at high temperatures.

1. A tungsten filament which had been exposed to fluorine for several minutes was slowly heated in vacuum and electron emission measured as a function of temperature. The temperature was raised to 2650°K, then slowly lowered. The electron emission on lowering the temperature was much greater at a given temperature than before heating but was not as high as the emission of tungsten which had never been exposed to fluorine. The work function of the fluorine covered tungsten is in the neighborhood of 5.6 e.v., but the data were not sufficiently reproducible to allow an accurate estimate of this quantity. The results are shown in Fig. 1.

2. Under the assumption that all fluorine molecules hitting the filament leave as atoms, ions, or molecules in equilibrium at the temperature of the filament, the electron affinity of fluorine, as calculated from Eq. (I-3), is given by

$$-\Delta E_0 = 4.574 \times 10^{-3} T_s (\log 100 i_t / i_e - \log P_r + 2 \log T_s + 3.338 \times 10^{-5} T_s + 7.711), \quad (1)$$

where P_r is the pressure of fluorine gas in the filament chamber, in microns.

[1] M. Metlay and G. E. Kimball, J. Chem. Phys. 16, 774 (1948), hereinafter referred to as I.

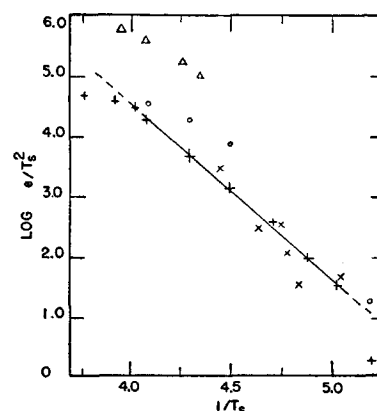[2] G. M. Murphy and J. E. Vance, J. Chem. Phys. 7, 806 (1939).

FIG. 1. Log electron emission over T^2 plotted against the reciprocal of the filament temperature. + temperature raised, filament fluorine covered in vacuum, O temperature lowered, immediately after above run, × in the presence of fluorine gas, and △ clean tungsten in vacuum.
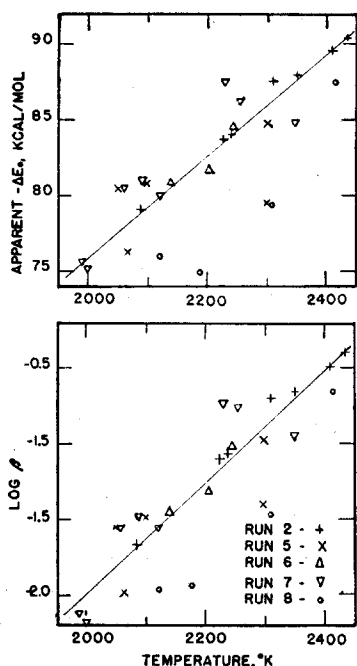
FIG. 2. Apparent electron affinity of fluorine, and logarithm of fraction of fluorine molecules dissociated, plotted against filament temperature.

If it is assumed that the fraction β of the molecules hitting the filament is dissociated, P_r in Eq. (1) must be replaced by βP_r, as in Part I. Using 95 kcal./mole[3] as an assumed value of the electron affinity of fluorine, we may calculate β from (1) as

$$-\log\beta = (95 + \Delta E_0)/4.574 \times 10^{-3} T_s. \qquad (2)$$

The values of β for the various runs are listed in Table I, and $\log\beta$ is plotted against temperature in Fig. 2. It is shown clearly there that the fraction of molecules dissociated increases exponentially with temperature.

3. The decrease in the diameter of the filament for different runs was measured. Table II lists, for each of several runs, the temperature T_s, the fluorine pressure P_s, the number z_w of tungsten atoms leaving the filament per cm² per second, and the ratio of z_F to z_w, where z_F is the number of F atoms striking one cm² of filament

[3] This value is the average of the results of Mayer and Helmholtz, Zeits. f. Physik **75**, 19 (1932), who find $-\Delta E_0 = 95.3$ kcal./mole, from calculations of Born cycles, and of Ionov, Comptes Rendus Acad. Sci. U.R.S.S. (Doklady), **28**, 512 (1940), who obtains $-\Delta E_0 = 94.7$ kcal./mole, from an investigation of the dissociation products of alkali fluorides on tungsten.

in one second in the form of F_2. It is seen that there is no appreciable trend of z_w with temperature or with pressure.

INTERPRETATION OF RESULTS

Roberts[4] presents evidence for the following picture of the adsorption of oxygen on tungsten in the temperature range 1100°K and 1700°K. The oxygen is first adsorbed in the form of a stable atomic layer, each adsorbed molecule occupying two adjacent tungsten atoms. When this layer is complete, the surface will contain about 8 percent of isolated tungsten atoms, which are not sites for adsorbed oxygen atoms. Adsorption then continues as molecules are adsorbed in the holes in the first layer. When these are filled, any further adsorption will be of molecules into a mobile third layer deposited on the first two layers. On heating the tungsten to 1700°K, the top two layers desorb, leaving only the stable atomic layer and the holes.

We shall now examine the experimental results described above in the light of this picture. It is

TABLE I. Experimental results for fluorine.

Run	T, °K	P, μ	$-\Delta E_0$	$-\log\beta$	β
2	2083	4.5	79.1	1.66	0.022
	2311	5.6	87.6	0.70	0.20
	2240	6.1	84.1	1.06	0.087
	2227	6.7	83.8	1.10	0.079
	2435	5.7	90.5	0.40	0.40
	2348	5.3	88.0	0.66	0.22
	2411	5.0	89.6	0.49	0.32
5	2067	3.0	76.3	1.98	0.01
	2300	2.8	79.5	1.40	0.04
			84.8	0.97	0.11
	2048	2.4	80.5	1.55	0.028
	2100	2.5	80.8	1.48	0.033
6	2206	2.1	81.7	1.32	0.048
	2243	1.9	84.5	1.02	0.096
	2139	1.1	80.9	1.45	0.035
7	1991	0.7	75.7	2.12	0.0076
	2000	1.1	75.2	2.17	0.0068
	2120	1.1	80.0	1.55	0.028
	2230	1.7	87.5	0.73	0.186
	2255	2.3	86.2	0.76	0.174
	2350	3.6	84.8	0.95	0.11
	2060	2.0	80.5	1.54	0.029
	2090	2.5	81.0	1.47	0.034
8	2309	1.2	79.5	1.47	0.034
	2414	1.4	87.7	0.66	0.22
	2122	1.8	76.0	1.96	0.011
	2181	3.4	75.0	1.94	0.012

[4] J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, 1939).

evident from the study of electron emission as a function of the temperature of the fluorine coated filament that an extremely stable layer is formed which does not desorb below 2600°K. This corresponds to Roberts' first layer. It would be expected that any holes in this film would be filled by fluorine molecules, corresponding to Roberts' second layer. At elevated temperatures, these might either desorb as such, followed by dissociation, or they might dissociate in situ, leaving one atom adsorbed and desorbing the other atom of the molecule. This latter process would cause the surface to be completely covered by the stable atomic first layer.

The investigation of the fraction of the fluorine molecules dissociated seems to indicate that the fluorine is adsorbed onto a layer corresponding to Roberts' third layer. The precise nature of this layer, in the case of fluorine, is not yet clear.

A plausible explanation of the high rate of loss of tungsten is inherent in this picture. The fluorine atoms are sufficiently small as compared to the internuclear distance of tungsten so that an occasional atom or molecule from the second layer can slip between the atoms of the first

TABLE II. Rate of loss of tungsten from the filament.

Run	T, °K	P, μ	z_w	z_F/z_w
2		6	7.0×10^{15}	566
3		2.4	8.4×10^{15}	190
7A	1990	1.0	7.3×10^{15}	90
7B	2120	1.2	1.1×10^{16}	72
7C	2250	2.4	1.25×10^{16}	128
7D	2350	3.0	1.03×10^{16}	194
7E	2075	2.4	1.13×10^{16}	140

layer, form chemical bonding with the tungsten, and sufficiently weaken the remaining tungsten-tungsten bonds so that the tungsten fluoride thus formed is readily evaporated.

CONCLUSION

Fluorine is found to form a very stable atomic layer on the surface of tungsten, which does not desorb below 2600°K. A less stable layer is believed to adsorb over the first layer. The fraction of the fluorine dissociated on the surface of the tungsten is exponential in temperature, and the rate of loss of tungsten from the surface is independent of temperature and of pressure, in the range 2000°K to 2400°K, and 1 to 6 microns of mercury pressure.

The Energy Levels and Thermodynamic Functions of the Fourth Power Oscillator

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The first six characteristic numbers of the reduced wave equation $\psi'' + (\lambda - \xi^4)\psi = 0$ have been calculated by a method of numerical integration. These values have been compared with the corresponding values obtained from the first, second, and third Wentzel-Kramers-Brillouin approximations. For the fourth, fifth, and sixth characteristic numbers, the third W.K.B. approximation is correct within 0.0001. The four thermodynamic functions — $(F-H_0)/RT$, $(H-H_0)/RT$, S/R, and C/R have been calculated over the range $h\nu_0/kT = 0$ to 10. A previously reported maximum in the heat capacity function, C/R, does not exist.

THE potential $V(x) = ax^4$ is intermediate between the square law potential of the simple harmonic oscillator and the rectangular potential of the particle in a one-dimensional box with infinitely high walls. For this reason alone the energy levels of the fourth power oscillator are of interest. In addition, some molecules may

contain a vibration with a fourth power potential. For example, the twisting motion of the bridge structure in the aluminum halide dimers and in diborane may be of this type. Bell[1] has discussed the energy levels and the heat capacity of the fourth power oscillator. There are, how-

[1] R. P. Bell, Proc. Roy. Soc. **A183**, 328 (1944).