PHYSICS

A. A. ARSHINOV and A. K. MUSIN

1958

SovietRxiv

Abstract

Full Text

PHYSICS

A. A. ARSHINOV and A. K. MUSIN

THERMIONIC EMISSION OF ELECTRONS FROM CARBON PARTICLES

(Presented by Academician V. N. Kondrat' ev, 10 VI 1957)

The question of the emission of electrons from carbon particles arose in connection with attempts to explain the anomalously high electron concentration observed ([1,2]) in rich hydrocarbon flames. This question was considered in work ([3]), in which, however, the reverse process—recombination of electrons with positively charged carbon particles—was not taken into account. In such a formulation the problem does not lead to a finite equilibrium value of the electron concentration.

Let us consider the emission of electrons from carbon particles with allowance for the reverse process. The rate of change of the electron concentration n_e, due to the processes of emission and recombination, will be

$$\frac{dn_e}{dt} = n\,\frac{AS}{e}\,T^2 \exp\left(-\frac{\varphi}{kT}\right) - \alpha n_e n_+, \tag{1}$$

where A is the emission constant; S is the surface area of the emitting particle; e is the electron charge; T is the absolute temperature; φ is the work function; k is Boltzmann' s constant; α is the recombination coefficient; n is the total concentration of carbon particles and n_+ is the concentration of charged carbon particles. We note that the Richardson–Dushman formula used in (1), derived for metals, is valid for graphite only approximately.

Considering all carbon particles identical and equivalent, one may write: $S = 4\pi r^2$, where r is the particle radius; $n_e = mn_+$, where m is the charge of the particle in units of e; $n_+ = n$ (by virtue of the equivalence of the particles); $\varphi = \varphi_0 + me^2/r$, where φ_0 is the initial work function, and the term me^2/r takes into account the increase in the work function due to the charge of the particle. Taking the cross section of the recombination process in the first approximation as equal to πr^2, we obtain $\alpha = \pi r^2 \bar{V}_e$, where $\bar{V}_e = (8kT/\pi m_e)^{1/2}$ is the electron velocity, and m_e is the electron mass.

Substituting into (1) the expressions for S, n_e, n_+, α, and φ, we obtain

$$\frac{dn_e}{dt} = n\pi r^2 \left[\frac{4AT^2}{e} \exp\left(-\frac{\varphi_0 + me^2/r}{kT}\right) - \left(\frac{8kT}{\pi m_e}\right)^{1/2} mn \right]. \tag{1'}$$

At equilibrium $dn_e/dt = 0$, and, consequently,

$$4AT^2 \exp\left(-\frac{\varphi_0 + me^2/r}{kT}\right) = em_0 n \left(\frac{8kT}{\pi m_e}\right)^{1/2}, \tag{2}$$

where m_0 is the charge of a carbon particle attained at equilibrium. Equation (2) is greatly simplified when $e^2 m_0/r \ll \varphi_0$, i.e., if the charge of the particle does not substantially increase the initial work function. In this case the equilibrium concentration of electrons $n_e^0 = m_0 n$ will be

$$n_e^0 = \frac{4AT^2 \exp(-\varphi_0/kT)}{e\,(8kT/\pi m_e)^{1/2}}, \tag{3}$$

i.e., n_e^0 depends neither on the number of particles nor on their sizes! This result, surprising at first glance, is readily explained if n_e^0 is regarded as the concentration (pressure) of saturated electron vapor over the solid carbon phase.

The methods of statistical thermodynamics make it possible to find n_e^0 from consideration of the equilibrium

$$\mathrm{C}\ leftarrows \mathrm{C}^+ + e^-, \qquad k = n_e^0,$$

where for the equilibrium constant k, or for n_e^0, the expression obtained is

$$n_e^0 = \frac{2(2\pi m_e kT)^{3/2}}{h^3} \exp\left(-\frac{\varphi_0}{kT}\right). \tag{4}$$

Formula (3) coincides with (4) if in (3) one substitutes the theoretical value of the Richardson constant $A = 4\pi m_e e k^2/h^3 = 120$ a/cm^2 deg^2. (For graphite the experimental value is $A = 48 \pm 25$ a/cm^2 deg^2 [4]. The difference from the theoretical value of A is associated mainly with reflection of electrons from the crystal surface.)

From (2) and (3) it follows that the equilibrium concentration of electrons n_e^*, with allowance for the correction for the increase in the work function, will be

$$n_e^* = n_e^0 \exp(-e^2 m_0/rkT). \tag{5}$$

Thus, at $T = \text{const}$, n_e^* is a function of the ratio of the particle charge m_0 to its radius r. From (5) one can find m_0/r if n_e^* is known. The electron concentration

n_e^* in rich $C_2H_2 - O_2$ flames was measured in [1]. Table 1 gives the values of n_e^* taken from [1], as well as: n_e^0, calculated by formula (4) for $\varphi_0 = 4.35$ eV [4]; m_0/r and $e^2 m_0/r$, found from (5), and $\varphi = \varphi_0 + e^2 m_0/r$—the work function at equilibrium.

Table 1

C_2H_2/O_2	T, °K	n_e^*, cm^{-3}	n_e^0, cm^{-3}	n_e^0/n_e^*	m_0/r, cm^{-1}	$e^2 m_0/r$, eV	φ, eV
1.5	3285	$3.47 \cdot 10^{10}$	$1.74 \cdot 10^{14}$	$5.02 \cdot 10^3$	$1.68 \cdot 10^7$	2.42	6.77
2.25	3195	$1.42 \cdot 10^{10}$	$1.09 \cdot 10^{14}$	$7.69 \cdot 10^3$	$1.71 \cdot 10^7$	2.46	6.81
4.0	3090	$6.44 \cdot 10^9$	$6.03 \cdot 10^{13}$	$9.38 \cdot 10^3$	$1.69 \cdot 10^7$	2.43	6.78

It is seen from Table 1 that at $T = 3300 \div 3100$°K the work function from carbon particles is ~ 6.8 eV, i.e., 2.45 eV greater than the initial work function $\varphi_0 = 4.35$ eV. This corresponds to $m_0/r = 1.7 \cdot 10^7$ cm^{-1}.

Table 2

r, cm	m_0	n, cm^{-3}	$\sum n_C$, cm^{-3}
10^{-7}	1.7	$2 \cdot 10^{10}$	10^{13}
10^{-6}	17	$2 \cdot 10^9$	10^{15}
10^{-5}	170	$2 \cdot 10^8$	10^{17}
10^{-4}	1700	$2 \cdot 10^7$	10^{19}

Table 2 gives: the values of the particle charge m_0 for different r, the concentration of carbon particles n, found from the relation $n_e^* = m_0 n$, for $T = 3285$°K, as well as the total number of carbon atoms $\sum n_C$ condensed in these particles.

Particles with $r < 10^{-6}$ cm, evidently, have not yet formed a crystalline structure* with a work function of 4.35 eV and, consequently, cannot effectively participate in emission. Particles with $r > 10^{-5}$ cm cannot provide the observed concentration n_e^*, since $\sum n_C$ for them exceeds the total carbon content in the flame, equal to $\sim 10^{18}$ atoms/cm^3. Thus, the electron concentration must be created mainly by particles with sizes—

* According to X-ray structural analysis data [5], in C_2H_2-flames the carbon particles consist of crystallites 13 Å wide and 21 Å long, with lattice constants $a = 4.21$ Å and $c = 7.1$ Å.

radii of the order of 10^{-6} cm, to which there corresponds a charge of several tens of electrons.

Let us consider the question of the time required to attain emission equilibrium. Integration of equation (2), under the assumption $\varphi' = \varphi_0 + e^2 m_0/r$ and $m|_{t=0} =$

0, gives the following expression for the charge of the particles as a function of time:

$$m = \frac{4\pi r^2 AT^2}{e} \exp\left(-\frac{\varphi'}{kT}\right) \frac{1-\exp(-\alpha nt)}{\alpha n}. \tag{6}$$

It follows from (6) that equilibrium is practically reached in a time $\tau = \frac{1}{n\alpha} = \frac{1}{n\pi r^2 \overline{V}_e} = \frac{m_0}{n_e^* \pi r^2 \overline{V}_e}$, where τ is an overestimate, since the emission rate is minimal at $\varphi' = \varphi_0 + e^2 m_0/r$. For $T = 3285^{\circ}$K and $r = 10^{-6}$ cm, $\tau = 4 \cdot 10^{-6}$ sec, i.e., equilibrium has time to become established under flame conditions, where the residence time of the particles is $\sim 10^{-3} \div 10^{-2}$ sec.

Received
3 VI 1957

References

1. K. E. Shuler, J. Weber, *J. Chem. Phys.*, **22**, 491 (1954).
2. T. M. Sugden, B. A. Thrush, *Nature*, **168**, 703 (1951).
3. V. I. Tverdokhlebov, DAN, **103**, 1049 (1955).
4. G. Glockler, J. W. Sausville, *J. Electrochem. Soc.*, **95**, 292 (1949).
5. U. Hofmann, D. Wilm, *Zs. Elektrochem.*, **42**, 504 (1936).

Note: Figure translations are in progress. See original paper for figures.