

## The Positive Column of the Nitrogen Arc at Atmospheric Pressure

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Extending earlier work by one of us,<sup>1</sup> a theory of the positive column in an arc has been developed, from considerations of energy balance, from which good values of nitrogen arc parameters are calculated from known properties of the gas. The power generation per unit volume is obtained in terms of the potential gradient, the electron mobility and the electron concentration. The electron concentration is computed with the aid of the Saha equation for thermal ionization. The power loss is calculated in terms of a generalized heat conductivity which includes the heat transport that results from the diffusion of dissociated atoms. Convection is neglected, so that the theory applies only to low current arcs in ordinary space or to arcs below 30 amperes in gravity-free space. Equating power generation and power loss leads to a differential equation that can be solved numerically once the center temperature is

known. Without solving the equation a change of variable is evident, which shows the potential gradient to be independent of the total power. This gives an arc equation of the Ayrton type. The arc is shown to be free from certain constraints which might otherwise set the center temperature. However, the center temperature is determined by introducing the additional consideration that the arc operates to make the power loss a maximum. The agreement with experiment is satisfactory. The inclusion of convection in a more complete theory is discussed, and it can be asserted that departure from the above simplified theory, for arcs of larger currents, is qualitatively of the type to be expected from the influence of convection. These results supply convincing evidence that the mechanism of the positive column of arcs is now understood.

### INTRODUCTION

THE electric arc can be divided into three distinct regions; one is near the cathode, one near the anode, and one between the two. The middle region is known as the positive column. The present investigation is concerned with the positive column of an arc running steadily between electrodes placed one above the other. The electrodes are of such a nature, or so cooled, as to prevent vapors or gases given off by them from being present in the positive column in greater than negligible amounts. In the arc at atmospheric pressure, the longitudinal potential gradient is known to be constant throughout the positive column; the apparent diameter of the arc is constant throughout the column, and the temperatures of both electrons and gas are several thousands of degrees.

Evidence for these statements can be found throughout the literature of the subject. Even for arcs less than ten millimeters in length, voltage *vs.* length plots show considerable straight portions for most of the current range investigated. This can be seen from the measurements taken by Nottingham<sup>2</sup> in air. Suits,<sup>3</sup> from the same

type of measurement and by a more direct method applied to a wide variety of arcs, concludes that the longitudinal potential gradient in the positive column is constant.

Suits<sup>3</sup> as a result of his measurements on arcs of various lengths states definitely that the arc diameter is independent of length over the positive column. Further evidence on this point is to be found from various photographs appearing in the literature on the subject. Even for arcs as short as six millimeters,<sup>4</sup> as can be seen from Nottingham's Fig. 4, an approximately uniform portion extends over several millimeters in the center.

A number of different methods have been employed for the measurement of temperatures in the positive column. Ornstein<sup>5</sup> and his co-workers have obtained values for both electron and gas temperatures from spectroscopic measurements. The electron temperatures were deduced from the relative intensities of atomic lines and of electronic bands. The gas temperatures were obtained from relative intensities of the rotational lines in the bands and of the vibrational band heads. From these measurements the indications are that, within experimental error, the electron and gas temperatures

<sup>1</sup> E. S. Lamar, *Phys. Rev.* **49**, 861 (1936).

<sup>2</sup> W. B. Nottingham, *Phys. Rev.* **28**, 764 (1926).

<sup>3</sup> C. G. Suits, *Phys. Rev.* **55**, 561 (1939).

<sup>4</sup> W. B. Nottingham, *J. Frank. Inst.* **206**, 52 (1928).

<sup>5</sup> L. S. Ornstein: *His Life and Work* (Utrecht, 1933).

are equal.<sup>6</sup> In air or nitrogen the value of each temperature is independent of current. The best spectroscopic measurements on d.c. arcs give temperatures in air ranging from 5700°K to 6700°K with an average of 6200°K.

Electron temperatures deduced from probe measurements are in disagreement with the spectroscopic values by as much as a factor of three in some cases.<sup>7</sup> It has been shown by Mason<sup>8</sup> that the probe constitutes a serious disturbing factor when introduced into the arc. Quantitative deductions from such probe measurements, therefore, remain open to criticism in the absence of further analysis.

Values of the gas temperature in the positive column have been deduced from indirect measurements of the gas density. Engel and Steenbeck<sup>9</sup> obtained the gas density from measurements of the absorption coefficient of soft x-rays and from the range of  $\alpha$  particles.<sup>10</sup> Ramsauer<sup>11</sup> performed similar measurements using 100-kv beta-rays. The values obtained from these density measurements were somewhat lower than the spectroscopic ones but hardly more than the probable experimental error.

The latest and perhaps the most reliable values of gas temperature are those deduced by Suits<sup>12</sup> from measurements of the velocity of sound through the arc. His value for nitrogen is 6100°K with little or no dependence on arc current.

Three concepts underlie the present theory of the arc positive column. First is the theory of thermal ionization following the Saha equation, introduced by Compton<sup>13</sup> and found not inconsistent with experimental observations. Second is the application of an energy-extreme principle, introduced into arc studies by Compton and

Morse<sup>14</sup> who, however, applied it differently and only to the region of the cathode. Third is the application of heat balance, earlier applied to the cathode region, but first applied with any rigor to the positive column by Lamar,<sup>1</sup> who also applied the energy-extreme principle to this region. Armed with further experimental evidence, Ornstein and Brinkmann<sup>15</sup> further justified the assumption of thermal ionization and the use of the Saha equation.

Energy balance equations have been used by many investigators.<sup>16</sup> In particular, Elenbaas by ingenious experiments was able to obtain sufficient boundary conditions to arrive at a satisfactory solution in the case of the high pressure mercury arc. Suits has enjoyed great success in correlating arc data from dimensional considerations following similar treatment of heat losses from solids.<sup>17</sup> At very low currents Lamar,<sup>1</sup> using an energy extreme hypothesis and no arbitrary constant, obtained temperature and power dissipation per unit length for the nitrogen positive column. The present paper carries forward this type of analysis in greater detail and precision.

#### SIMPLE THEORY OF THE POSITIVE COLUMN

Following Compton,<sup>13</sup> the arc current density can be written as

$$J = J_+ + J_- = n_+ e \mu_+ E + n_- e \mu_- E. \quad (1)$$

The absence of an appreciable second derivative of the potential leads from Poisson's equation to the equality of  $n_+$  and  $n_-$ . Hence, since the electron mobility greatly exceeds that of the positive ions, the first term on the right of Eq. (1) can be neglected and with it the necessity for subscripts in the second. The power generation per unit length in the ring element between  $r$  and  $r + dr$ , therefore, can be written as

$$dW = 2\pi J E r dr = 2\pi E^2 n e \mu r dr. \quad (2)$$

<sup>6</sup> R. Mannkopf, *Zeits. f. Physik* **86**, 161 (1933); H. Witte, *Zeits. f. Physik* **88**, 415 (1934).

<sup>7</sup> W. B. Nottingham, *J. Frank. Inst.* **206**, 43 (1928); **207**, 299 (1929).

<sup>8</sup> R. C. Mason, *Phys. Rev.* **51**, 28 (1937).

<sup>9</sup> A. von Engel and M. Steenbeck, *Phys. Rev.* **37**, 1554 (1931); *Wiss. Veroff. Siemens K.* **XII**, 1, 81 (1933).

<sup>10</sup> A. von Engel and M. Steenbeck, *Wiss. Veroff. Siemens K.* **XII**, 1, 74 (1933).

<sup>11</sup> C. Ramsauer, *Electrotech. u. Maschinenbau* **51**, 189 (1933).

<sup>12</sup> C. G. Suits, *Physics* **6**, 190, 196, 315 (1935); *Proc. Nat. Acad.* **21**, 48 (1935); *G. E. Rev.* **39**, 194 (1936).

<sup>13</sup> K. T. Compton, *Phys. Rev.* **21**, 266 (1923); *J. A.I.E.E.* **46**, 868 (1927).

<sup>14</sup> K. T. Compton and P. M. Morse, *Phys. Rev.* **30**, 305 (1927).

<sup>15</sup> L. S. Ornstein and H. Brinkmann, *Physica* **1**, 797 (1934).

<sup>16</sup> Ter Horst, Brinkmann and Ornstein, *Physica* **2**, 652 (1935); W. Elenbaas, *Physica* **1**, 211, 673 (1934); **2**, 757 (1935); B. Kirschstein and F. Koppelman, *Wiss. Veroff. Siemens K.* **XVI**, 3, 56 (1937); C. G. Suits, *Phys. Rev.* **52**, 245 (1937); *G. E. Rev.* **39**, 194 (1936); *Physics* **6**, 196 (1935); C. G. Suits and H. Poritsky, *Phys. Rev.* **52**, 136 (1937).

<sup>17</sup> W. J. King, *Mech. Engin.* May (1932).

The assumption of thermal ionization as the only process contributing to the electron concentration  $n$  permits  $n$  to be expressed as a function of temperature only, by the Saha<sup>18</sup> equation. The electron mobility  $\mu$  is computed from kinetic theory<sup>19</sup> and hence is a function of temperature only. Eq. (2) can be rewritten, therefore, as

$$dW = 2\pi E^2 F r dr, \quad (3)$$

where  $F = ne\mu$ , a function of temperature only.

In the nitrogen positive column there are five processes by means of which energy is lost: (1) radiation; (2) the radial drift of ions and electrons, each pair taking with it the ionization energy; (3) convection; (4) the diffusion of atoms out from the arc, each pair taking with it the dissociation energy of the molecule; and (5) thermal conduction. Concerning radiation, Holm and Lotz,<sup>20</sup> from measurements of the total radiation from the positive column of a long carbon arc with large alternating currents flowing, give the radiation loss as five percent at 30 amperes. Extrapolation of their experimental curve below 10 amperes indicates completely negligible radiation loss in this range. Hence radiation is neglected here. As will be seen later, the radial drift of ions and electrons accounts for only negligible power loss and hence is neglected. Convection within the radius occupied by the arc, discussed later, is neglected in the simple theory, making this first treatment applicable only to cases in which convection losses in the arc are known to be small. The term representing the power loss by diffusion of atoms has the form of a conduction term and hence is included in a generalized conductivity  $\Theta$ .

Neglecting convection, therefore, the power loss can be written as

$$dW = -2\pi \frac{d}{dr} \left( r\Theta \frac{dT}{dr} \right) dr = 2\pi E^2 F r dr, \quad (4)$$

which, integrated and rearranged, gives

$$dT/dr = -(E^2/r\Theta) \int_0^r F r dr. \quad (5)$$

It is possible to integrate Eq. (5) for any value of  $E$  to give the temperature distribution,  $W$  and hence the current  $I$ . The temperature gradient in the arc center must be zero, however, and the temperature  $T_c$  known. The problem then resolves itself into one of determining this temperature  $T_c$  along the axis of the positive column.

In a pure conduction problem of this kind one difficulty arises immediately. The boundary condition  $dT/dr = 0$  must be satisfied when  $T = T_0$ , the ambient temperature. This cannot be done unless  $W$  is zero or  $T_c$  is infinity. Hence, although convection is neglected within the radius occupied by the arc, it must be considered outside of this radius in any argument for determining  $T_c$ .

Further information for use in determining  $T_c$  can be obtained from consideration of a similar thermal problem; namely, that of the heat losses from solid cylinders immersed in a fluid.

Dimensional arguments<sup>17</sup> applied to heat losses from solid cylinders lead to the conclusion that

$$H/K = f(g\alpha\theta d^3/\nu^2), \quad (6)$$

where  $H$  is the heat loss per unit length per degree temperature excess;  $K$ , the thermal conductivity;  $g$ , the acceleration of gravity;  $\alpha$ , the thermal expansion coefficient of the fluid;  $\theta$ , the temperature excess of cylinder above surroundings;  $d$ , the cylinder diameter; and  $\nu$ , the kinematic viscosity (the ratio of viscosity to density).

This formula has been applied successfully to cases in which  $\theta$  is small in comparison with  $T$ , with  $\alpha$ ,  $K$  and  $\nu$  evaluated at the average temperature. A similar relation has been found by Suits and Poritsky to hold for the arc if  $\alpha$  is evaluated at ambient temperature, and  $K$  and  $\nu$  at the temperature of the arc.

From the plot of  $H/K$  vs.  $g\alpha\theta d^3/\nu^2$  presented in King's review<sup>17</sup> it can be seen that  $H/K$  does not change very rapidly with changes in the abscissa. This should be true for the arc also.

The arc differs from the solid cylinders just considered in that it has no sharp solid boundary. Hence it may be possible to find a diameter  $d$ , which includes the arc and at which the dimensional relationship is satisfied, for a wide range of assumed values of  $T_c$  rather than for only one. This seems to be true of the atmospheric arc

<sup>18</sup> R. H. Fowler, *Statistical Mechanics* (Cambridge, 1929), p. 281.

<sup>19</sup> K. T. Compton and I. Langmuir, *Rev. Mod. Phys.*, **2**, 218 (1930).

<sup>20</sup> R. Holm and A. Lotz, *Wiss. Veroff. Siemens K.* **XIII**, 2, 87 (1934).

and hence so far as external conditions are concerned, this arc is free to select any value of  $T_c$  within the allowed range. It is by no means certain that arcs having small values of  $g\alpha\theta d^3/\nu^2$  at pressures other than atmospheric can be treated without regard for the boundary condition at  $T_0$ .

In order to fix the value of  $T_c$  within the allowed range it is assumed that the arc will adjust itself so as to operate with extreme power dissipation. The adjustment is possible because the outer boundary condition does not constitute a constraint. The integration indicated by Eq. (5) was carried out numerically for each of a number of assumed values of  $T_c$ . The values of  $W$  resulting from these integrations were plotted as a function of  $T_c$ . Within the range of temperatures permitted by the absence of constraints, there is one maximum and one minimum. The maximum provides better agreement with experiment than does the minimum. Before carrying out the integration it was necessary to compute the two functions  $F$  and  $\Theta$  occurring in Eq. (5).

The function  $F = ne\mu$  is a function of temperature only. The mobility  $\mu$ , occurring in  $F$ , was computed by means of Eq. (107) in Compton and Langmuir's paper.<sup>19</sup> For molecular nitrogen the value of  $\lambda_0$ , given on page 208 of that article, was used. The kinetic theory mean free path for atomic nitrogen is not known. It seems reasonable to suppose, however, that the ratios of atomic to molecular mean free paths should not differ greatly from gas to gas. For hydrogen this ratio is known to be 1.183. If this ratio is used and each gas is weighted according to its partial pressure in obtaining  $\lambda_0$ , the mobility of a mixture of atomic and molecular nitrogen turns out to be

$$\mu = \{4.52(10^2)T^{\frac{1}{2}}/P\} \{1 + 0.183P_a/P\}, \quad (7)$$

where  $\mu$  is in cm<sup>2</sup>/sec. volt,  $P$  is the total gas pressure, and  $P_a$  the partial pressure of atoms; both pressures are in atmospheres.

Fowler<sup>18</sup> writes the Saha equation for a single gas as

$$\frac{n^- n^+}{n} = \frac{\omega^- \omega^+}{\omega} \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} e^{-V_{ie}/kT}, \quad (8)$$

where  $n^-$ ,  $n^+$  and  $n$  are the concentrations of

electrons, ions and neutral gas, respectively. The  $\omega$ 's are the respective statistical weights,  $V_i$  is the ionization potential, and the other symbols have their usual meanings. The derivation of Eq. (8) involves the assumption that the neutral gas has no excited states below ionization and that the positive ions have only a ground state. With nitrogen over the temperature range considered here, the population of the ground state greatly exceeds the combined populations of the other states for both neutral gas and positive ions. Eq. (8), in which the  $\omega$ 's are the multiplicities of the respective ground states, can then be used.

Substituting for the various statistical weights and introducing subscripts for the molecular and atomic gases, we obtain

$$\frac{n^- n_m^+}{n_m} = 4 \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} e^{-V_m e/kT}$$

and

$$\frac{n^- n_a^+}{n_a} = \frac{1}{2} \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} e^{-V_a e/kT}.$$

If we remember that  $n_m^+ + n_a^+ = n^-$ , and drop the  $-$  superscript,

$$n = \left( \frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} (4n_m e^{-V_m e/kT} + \frac{1}{2}n_a e^{-V_a e/kT})^{\frac{1}{2}}. \quad (9)$$

Both  $n_m^+$  and  $n_a^+$  are known to be small in comparison with  $n_m$  and  $n_a$ . Hence the latter two can be computed directly from the partial pressures of atoms and molecules, respectively. The ionization potentials  $V_m = 16.5$  volts<sup>21</sup> and  $V_a = 14.5$  volts<sup>22</sup> were selected. Numerically, therefore,

$$n = 3.006(10^{18})T^{\frac{3}{2}} \times (P_a e^{-168300/T} + 8(P - P_a)e^{-191500/T})^{\frac{1}{2}} \quad (10)$$

and finally,

$$F = 2.17(10^2)T^{\frac{3}{2}} \times \{P_a e^{-168300/T} + 8(P - P_a)e^{-191500/T}\}^{\frac{1}{2}} \times (1 + 0.183P_a/P)/P. \quad (11)$$

<sup>21</sup> W. Jevons, *Band Spectra of Diatomic Molecules* (Cambridge, 1932), p. 81.

<sup>22</sup> R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932), p. 293.

The partial pressure  $P_a$  was computed from the data of Giaque and Clayton,<sup>23</sup> a plot of which yields the equilibrium constant

$$K = P_a^2/P_m = 1.36(10^7)e^{-94700/T}. \quad (12)$$

Since  $P_a + P_m = P$ , we have

$$P_a = (K/2)\{(1+4P/K)^{1/2} - 1\}. \quad (13)$$

The functions  $F$ ,  $P_a$  and  $n$  are given in Table I computed for a total pressure of one atmosphere.

The generalized conductivity  $\Theta$  is the sum of two terms, one the ordinary thermal conductivity and the other a term contributed by atomic diffusion with its accompanying energy transfer. The gas under consideration is, of course, a mixture of molecules and atoms. With regard to the ordinary conductivity, a sufficiently good approximation for the mixture is given by an average of the separate conductivities of the two gases in the mixture, each weighted in proportion to its partial pressure.<sup>24</sup> The diffusion term will be considered later.

Measurements of thermal conductivity are not available at extremely high temperatures.

<sup>23</sup> W. F. Giaque and J. D. Clayton, J. Am. Chem. Soc. **55**, 4887 (1933).

<sup>24</sup> E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, 1938), p. 183.

Furthermore, there are difficulties inherent in the experiments which limit the reliability of thermal conductivity measurement in gases even at easily available temperatures. Hence, following Langmuir<sup>25</sup> the conductivity is obtained by means of the kinetic theory relationship connecting conductivity and viscosity, i.e.,  $K = \epsilon\eta C_V$ . Here  $\eta$  is the viscosity,  $C_V$  is the specific heat at constant volume, and  $\epsilon = \frac{1}{4}(9\gamma - 5)$ , where  $\gamma$  is the ratio of specific heats.<sup>26</sup>

Viscosity measurements are available for molecular nitrogen up to about 1000°K. Two different formulas have been considered for use in extrapolating these data to higher temperatures: the familiar Sutherland formula, and that due to Hassé and Cook.<sup>27</sup> The first of these has been employed here, since its use provides better agreement with experiment than does the second. Constants obtained from Landolt-Bornstein give the formula,

$$\eta = 138(10^{-7})T^{3/2}/(T+104.7). \quad (14)$$

The values of  $\eta$  given by the Sutherland formula are lower than those given by Hassé

<sup>25</sup> I. Langmuir, Phys. Rev. **34**, 401 (1912).

<sup>26</sup> J. H. Jeans, *Dynamical Theory of Gases* (Cambridge, 1925), p. 302.

<sup>27</sup> H. R. Hassé and W. R. Cook, Proc. Roy. Soc. **A125**, 196 (1929).

TABLE I. Values of the current density per unit potential gradient  $F(T)$ ; atomic nitrogen pressure  $P_a$ ; electron concentration  $n$ ; and generalized conductivity  $\Theta$ .

$T^\circ\text{K}$	$F(T)$ AMP./VOLT-CM	$P_a$ ATMOSPHERE	$n$ (CM) <sup>-3</sup>	$\Theta(T)$ WATT/CM-DEG.
2900	$1.160 \times 10^{-9}$	$2.99 \times 10^{-4}$	$2.987 \times 10^5$	$1.235 \times 10^{-3}$
3100	$1.065 \times 10^{-8}$	$8.454 \times 10^{-4}$	$2.653 \times 10^6$	$1.309 \times 10^{-3}$
3300	$7.612 \times 10^{-8}$	$2.170 \times 10^{-3}$	$1.846 \times 10^7$	$1.418 \times 10^{-3}$
3500	$4.437 \times 10^{-7}$	$4.906 \times 10^{-3}$	$1.039 \times 10^8$	$1.579 \times 10^{-3}$
3700	$2.160 \times 10^{-6}$	$1.015 \times 10^{-2}$	$4.916 \times 10^8$	$1.829 \times 10^{-3}$
3900	$9.144 \times 10^{-6}$	$1.949 \times 10^{-2}$	$2.023 \times 10^9$	$2.205 \times 10^{-3}$
4100	$3.390 \times 10^{-5}$	$3.496 \times 10^{-2}$	$7.299 \times 10^9$	$2.750 \times 10^{-3}$
4300	$1.132 \times 10^{-4}$	$5.922 \times 10^{-2}$	$2.368 \times 10^{10}$	$3.504 \times 10^{-3}$
4500	$3.382 \times 10^{-4}$	$9.454 \times 10^{-2}$	$6.873 \times 10^{10}$	$4.473 \times 10^{-3}$
4700	$9.293 \times 10^{-4}$	$1.438 \times 10^{-1}$	$1.832 \times 10^{11}$	$5.646 \times 10^{-3}$
4900	$2.358 \times 10^{-3}$	$2.086 \times 10^{-1}$	$4.500 \times 10^{11}$	$6.940 \times 10^{-3}$
5100	$5.532 \times 10^{-3}$	$2.888 \times 10^{-1}$	$1.024 \times 10^{12}$	$8.218 \times 10^{-3}$
5300	$1.221 \times 10^{-2}$	$3.822 \times 10^{-1}$	$2.174 \times 10^{12}$	$9.276 \times 10^{-3}$
5500	$2.520 \times 10^{-2}$	$4.835 \times 10^{-1}$	$4.329 \times 10^{12}$	$9.894 \times 10^{-3}$
5700	$4.890 \times 10^{-2}$	$5.860 \times 10^{-1}$	$8.114 \times 10^{12}$	$9.952 \times 10^{-3}$
5900	$8.987 \times 10^{-2}$	$6.811 \times 10^{-1}$	$1.441 \times 10^{13}$	$9.393 \times 10^{-3}$
6100	$1.563 \times 10^{-1}$	$7.633 \times 10^{-1}$	$2.435 \times 10^{13}$	$8.417 \times 10^{-3}$
6300	$2.595 \times 10^{-1}$	$8.293 \times 10^{-1}$	$3.937 \times 10^{13}$	$7.287 \times 10^{-3}$
6500	$4.135 \times 10^{-1}$	$8.791 \times 10^{-1}$	$6.127 \times 10^{13}$	$6.205 \times 10^{-3}$
6700	$6.369 \times 10^{-1}$	$9.154 \times 10^{-1}$	$9.243 \times 10^{13}$	$5.320 \times 10^{-3}$
6900	$9.309 \times 10^{-1}$	$9.409 \times 10^{-1}$	$1.326 \times 10^{14}$	$4.664 \times 10^{-3}$
7100	$1.383 \times 10^0$	$9.581 \times 10^{-1}$	$1.936 \times 10^{14}$	$4.178 \times 10^{-3}$
7300	$1.967 \times 10^0$	$9.702 \times 10^{-1}$	$2.711 \times 10^{14}$	$3.862 \times 10^{-3}$
7500	$2.743 \times 10^0$	$9.786 \times 10^{-1}$	$3.726 \times 10^{14}$	$3.653 \times 10^{-3}$

and Cook, and undoubtedly the truth is somewhere between. The use of the Sutherland formula together with a high estimate of the conductivity of atomic nitrogen leads to a reasonable value for the net conductivity.

The specific heat  $C_V$  was obtained from the values of  $C_P$  given by Giauque and Clayton<sup>28</sup> up to 5000°K. A plot of the data shows little curvature at that temperature. No great error was anticipated, therefore, in extrapolating to higher temperatures.

Using subscript 1 for quantities characteristic of atomic, and 2 for those characteristic of molecular, nitrogen, we may write

$$\frac{K_1}{K_2} = \frac{9\gamma_1 - 5}{9\gamma_2 - 5} \frac{\eta_1}{\eta_2} \frac{C_{V1}}{C_{V2}} \quad (15)$$

Simple kinetic theory relationships were used in evaluating this ratio, i.e.,  $\gamma_1 = 5/3$ ;  $\gamma_2 = 7/5$ ;  $C_{V1} = 3R/2M_1$ ;  $C_{V2} = 5R/2M_2$ , and

$$\eta_1/\eta_2 = (M_1/M_2)^{1/2} d_2^2/d_1^2.$$

The ratio  $d_2^2/d_1^2$ , as before, is taken as 1.183. Putting in the remaining constants gives  $K_1/K_2 = 1.33$ . The argument, however, does not justify use of more than two significant figures. As was stated earlier, the ordinary conductivity arrived at by using the Sutherland formula does not increase with temperature with sufficient rapidity to conform with experimental data. This deficiency can be approximately compensated for by increasing the ratio of atomic to molecular conductivities. This is done and the ratio is reasonably taken as 1.5 instead of the 1.33 computed from kinetic theory. Hence

$$K = K_2(1 + 0.5P_a/P). \quad (16)$$

The number of atoms diffusing across unit area per second is given by Chapman<sup>28</sup> as  $ND$  grad.  $(n_a/N)$  in the absence of gradients of temperature or total pressure. In this formula  $N$  is the total gas concentration,  $D$  the coefficient of ordinary diffusion, and  $n_a$  the atomic concentration. In the present case  $n_a$  is a function of temperature only and hence the diffusion term can be written as  $ND(d/dT)(n_a/N)dT/dr$ . On substituting for  $N$  and for  $n_a$  in terms of  $P$  and  $P_a$ ,

respectively, this becomes

$$[73.85(10^{20})P/T]D(d/dT)(P_a/P).$$

This term does not include so-called thermal diffusion, which is neglected here for reasons to be presented later. Each pair of atoms diffusing carries with it the dissociation energy  $2q$ . Hence the generalized conductivity (the coefficient which multiplies the temperature gradient) becomes

$$\Theta = K + \frac{73.85(10^{20})P}{T} qD \frac{d}{dT} (P_a/P). \quad (17)$$

Of the quantities appearing in Eq. (17)  $K$  has been discussed already. The dissociation energy  $2q$  was taken as 7.90 electron volts per molecule.<sup>28</sup> The coefficient of diffusion has been calculated by Amdur<sup>29</sup> for the case of hydrogen, following Enskog and Chapman. The formula given there is

$$D_{12} = \frac{3R^3 T^{3/2}}{8(2\pi)^{1/2} N_1 \{ \frac{1}{2}(d_1 + d_2) \}^2} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2} \times \frac{1}{P} \left( \frac{1.0364 - 0.0303\alpha}{1 + C_{12}/T} \right), \quad (18)$$

where  $N_1$  is Avogadro's number;  $R$  is the gas constant;  $d_1$  and  $d_2$  the atomic and molecular diameters, respectively;  $M_1$  and  $M_2$  the corresponding atomic weights;  $P$  the total pressure, and  $\alpha$  the degree of dissociation. The constant  $C_{12}$  is the Sutherland constant for the mixture and is given by

$$C_{12} = \frac{(C_1 C_2)^{1/2}}{\{ \frac{1}{2} [(d_1/d_2)^{1/2} + (d_2/d_1)^{1/2}] \}^5}. \quad (19)$$

Equation (18) is applied here to obtain the diffusion coefficient of nitrogen. From viscosity data Landolt-Bornstein give  $d_2 = 3.90\text{A}$ . The atomic diameter is not given but is computed here on the assumption that the ratio  $d_2/d_1$  is the same for nitrogen as for hydrogen. As was mentioned earlier, the ratio is given by Amdur as 1.088. An average value of  $\frac{1}{2}$  is taken for  $\alpha$ . Since  $\alpha$  goes from 0 to 1, the maximum error thus introduced is 1.5 percent. Assuming that  $C_1/C_2$

<sup>28</sup> S. Chapman, Phil. Trans. 217, 158 (1918).

<sup>29</sup> I. Amdur, J. Chem. Phys. 4, 339 (1936).

is the same for nitrogen as for hydrogen, and using  $C_2=104.7$ , we obtain  $C_1=87.8$ . Thus,  $C_{12}=96.0$  from Eq. (19). Putting in the other numerical factors gives, finally,

$$D = \frac{44.1(10^{-6})T^{\frac{3}{2}}}{P(1+96/T)} \quad (20)$$

and hence

$$\Theta = K + 0.205 \frac{T^{\frac{3}{2}}}{1+96/T} \frac{d}{dT} (P_a/P). \quad (21)$$

Values of  $\Theta$ , computed with the aid of Eq. (21) for  $P=1$  atmosphere, are presented in Table I. Eq. (21) is a Sutherland type of equation. As was mentioned earlier, the Sutherland equation gives values of the viscosity too low at high temperatures. Since the diffusion coefficient is proportional to the viscosity, the diffusion coefficient also should be too low at high temperatures. Thermal diffusion is opposite in direction to ordinary diffusion and is neglected here deliberately to compensate approximately for the diffusion deficiency known to exist.

The radial diffusion of electrons and ions is limited by the rate at which ions diffuse out. The coefficient of diffusion for the ions is about the same as for the atoms. The ionization potential is of the same order of magnitude as the dissociation energy expressed in electron volts, so that each pair of electron and ion carries with it about the same energy as does a pair of atoms. The concentration gradient of electrons and ions is small in comparison with that of the atoms, as can be seen from Table I. Hence the power carried out by electrons and ions can be neglected in comparison to that lost by generalized conduction.

Instead of carrying out the integration indicated by Eq. (5) a change of variable was introduced, namely,  $x=Er$ . With this change Eq. (5) becomes

$$dT/dx = -(1/x\Theta) \int_0^{\infty} Fx dx, \quad (22)$$

and  $W$ , the power input per unit length, becomes

$$W = EI = 2\pi \int_0^{\infty} Fx dx, \quad (23)$$

Hence Eq. (23) leads to the arc characteristic  $E = \text{const}/I$ , an equation of the Ayrton type, for cases in which convection heat losses within the arc are small in comparison with those due to conduction.

Equation (22) was integrated numerically in order to evaluate the constant occurring in Eq. (23), starting with a number of different assumed values of  $T_c$ , the center temperature. In the calculation of  $dT/dx$ , the values of  $x$  and  $F$  characteristic of the center of a zone of width  $dx$  were used in the numerator of Eq. (22). In the denominator of Eq. (22) the values of  $x$  and  $\Theta$  were characteristic of the edge of the zone. The resulting value of  $dT/dx$  referred to the edge of the zone, and its use in computing the temperature of the center of the next zone amounted to a three-term Taylor expansion of  $\Delta T$ .

#### RESULTS AND CONCLUSIONS

The values of  $W$  resulting from the integrations described above are presented as a function of  $T_c$  in Fig. 1. Any inaccuracy in the function  $\Theta$  appears directly as an inaccuracy in  $W$ . Inaccuracies in  $F$  appear in  $W$  to some power smaller than the first. This is easy to see, since a decrease in  $F$  both decreases the contribution of each zone to the power integral and increases the number of zones contributing by altering the temperature distribution.

There are two extremes represented in Fig. 1, one maximum and one minimum. Of these the maximum provides the better agreement with experiment.

The results of the simple theory should apply to cases in which convection is negligible, i.e., when  $g\alpha\theta d^3/\nu^2$  is small. This variable can be made small by decreasing the arc diameter, which is done by going to low currents. In Fig. 2  $W$  is plotted as a function of  $I$ . The horizontal line, curve  $A$ , is the theoretical curve and the other, curve  $B$ , is experimental. The solid line was obtained from Suits's data for pure nitrogen. The vertical lines represent unpublished data taken by Mr. J. J. Hopkins in this laboratory. The length of each vertical line indicates the probable error. In the figure the experimental curve approaches the theoretical at low currents, and

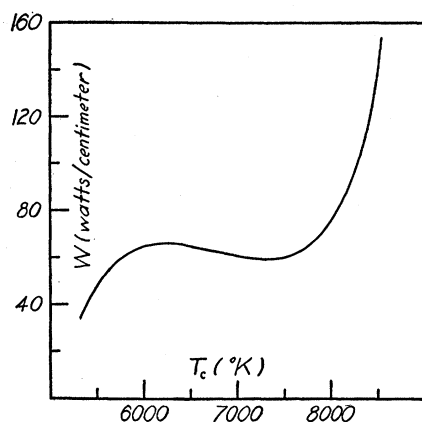


FIG. 1. Power loss per unit length,  $W$ , as a function of axial temperature,  $T_c$ .

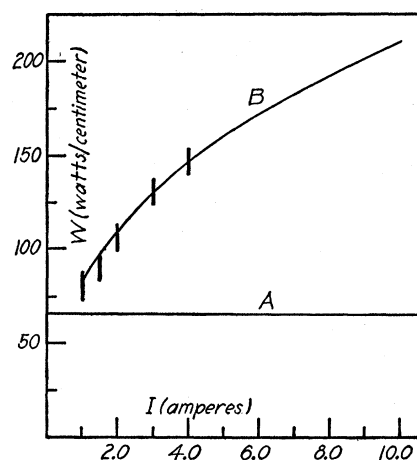


FIG. 2. Power loss per unit length,  $W$ , as a function of current,  $I$ .

the two coincide within experimental error, if the former is extrapolated to zero current.

The temperature distribution is shown by the plot of  $T$  vs.  $x$  in Fig. 3. Experimentally, the arc appears to have a well-defined edge, so that the apparent arc diameter can be determined either visually or photographically. Lacking values for the light emitted from unit volume of the arc as a function of temperature, this diameter has not been determined from theory. It has been found,<sup>15</sup> however, that the product of the visual cross-sectional area, the electric intensity  $E$ , and the  $F$  value characteristic of the measured temperature equals the measured current. This being the case, the apparent arc diameter should equal the theoretical root-mean-square diameter defined by Eq. (24) below.

$$d^2 = 4 \int_0^\infty Fr^3 dr / \int_0^\infty Fr dr. \quad (24)$$

In the literature one usually finds values of current density  $J$  as a function of total current rather than values of  $d$ . Remembering that  $x = Er$  and  $W = EI$ , we find Eq. (24) leads to

$$J = W^2 / \pi \langle x^2 \rangle_{Av} I = 9.65 / I, \quad (25)$$

where  $\langle x^2 \rangle_{Av}$  is the average value of  $x^2$ .

A plot of Eq. (25) is shown as curve A, Fig. 4. Curve B is a plot of the experimental values taken from Suits' paper.<sup>3</sup> The comparison of theoretical and experimental current densities is

difficult, for several reasons. In the first place, one would like experiments below one ampere in order to see whether or not the trend toward increased current density at decreased currents is anything like as marked experimentally as theoretically. In the second place, errors in the function  $F$  appear directly in computations of current density. These errors may be quite large because of uncertainties in the mobility and because of the fact that slight changes in temperature are amplified in changes in  $F$ .

The value of the function  $F$  required for the average current density given by Eq. (25) is that corresponding to a temperature of 6080°K. This temperature agrees remarkably well with the value of 6100°K given by Suits<sup>12</sup> as the temperature of the atmospheric arc in nitrogen determined from measurements of the velocity of sound. The center temperature  $T_c$ , on which the computations are based, is that temperature at which the maximum in  $W$  occurs, namely, 6200°K, again not far from the 6100°K given by Suits.

#### EFFECT OF CONVECTION\*

The variable  $g\alpha\theta d^3/\nu^2$ , which brings in convection effects, can be made small by effectively

\* Note added in proof.—Dr. Joseph Slepian has kindly pointed out that although  $g\alpha\theta d^3/\nu^2$  must be small, it cannot be zero if the present theory is to apply. In future experiments it will be interesting to see how far  $g$  can be reduced without the need for considering longitudinal changes in the positive column.



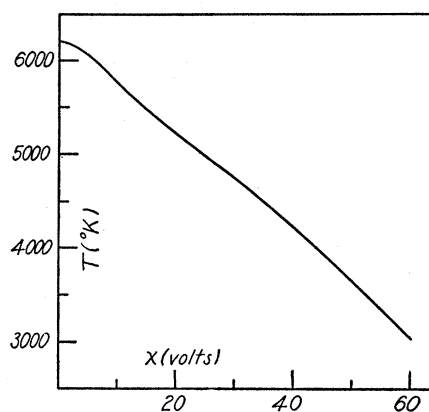


FIG. 3. Temperature distribution curve—temperature  $T$  as a function of  $x = Er$ , the product of longitudinal potential gradient and radius.

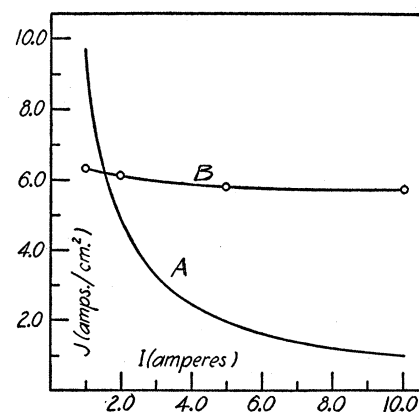


FIG. 4. Current density,  $J$ , as a function of current,  $I$ .

reducing the acceleration of gravity. The present theory should apply, therefore, to the results of experiments performed in gravity-free space. Steenbeck,<sup>30</sup> in a most ingenious set of experiments, has investigated an arc operating in a freely-falling container. His measurements were for air, not nitrogen, and were more qualitative than quantitative.

The air and nitrogen arcs do not differ greatly one from the other. Hence a comparison of Steenbeck's experiments in air with the present theory developed for nitrogen should at least prove instructive. Steenbeck concludes that the arc drop is less in gravity-free space than in ordinary space and mentions a factor of 2 or 3. His current range was from 1 to 8 amperes. He does not state at which of the various currents the factor of 2 or 3 is observed. It is interesting to note, however, that in Fig. 2 the experimental and theoretical values of  $W$  observed at 8 amperes bear the ratio, one to the other, of almost exactly 3. The diameter of the arc is observed by Steenbeck to increase when gravity is removed. The current density corresponding to a total current of 7 or 8 amperes is less than 1 amp./cm<sup>2</sup>. The theoretical value observed at 8 amperes in Fig. 4 is 1.2 amp./cm<sup>2</sup>. For currents below 4 amperes Steenbeck gives the current density as somewhere between 1 and 3 amp./cm<sup>2</sup>. Fig. 4 shows 2.4 amp./cm<sup>2</sup> at 4 amperes. If we consider the un-

certainities in the theoretical determination of current density and the qualitative nature of the experiments, the agreement seems satisfactory.

From Steenbeck's measurements it is safe to conclude that the theoretical results show the same trends as do the experiments with respect to the influence of convection, and that theory and experiment are not in quantitative disagreement. Quantitative measurements in nitrogen are greatly needed. In a private communication Dr. Suits has expressed an interest in such measurements, and it is sincerely hoped that he will carry them out.

A few preliminary computations on the arc at 10 atmospheres indicates about 80 watts per centimeter for  $W$ . The curve of  $W$  vs.  $T_c$  is almost flat over a wide temperature range. Hence the determination of  $T_c$  and of  $J$  awaits further computations.

Some attempts have been made at atmospheric pressure with a view toward including convection in developing a more complete theory of the arc. To date several empirical functions have been tried for representing convection heat loss. Each is subject to certain restrictions as to form, imposed by dimensional arguments, and hence none are entirely arbitrary. Any one of the three functions tried is satisfactory within the arc, but none of them behave properly at large radii. Work is still in progress, however, and it is hoped that an entirely satisfactory function will be developed before very long.

<sup>30</sup> M. Steenbeck, *Physik. Zeits.* **38**, 1019 (1937).

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PHYSICAL REVIEW

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## On the Calculation of Polarizabilities and Van der Waals Forces for Atoms in S States

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The perturbation scheme of Møller and Plesset, which has as its basis a complete set of solutions of the Fock single-electron differential-integral equation, is extended to the calculation of atomic polarizabilities and van der Waals force constants. The present treatment differs in three respects from the previous treatments of Kirkwood and Buckingham. First, the Hartree-Fock model is used consistently throughout the calculation. Additional functions are introduced to complete the set of single-electron functions. Sum rules are developed for these functions with the aid of their common Hamiltonian. These replace the Kuhn-Reiche sum rules, which do not apply in their usual form. Second, atomic polarizabilities are expressed as a

sum of sums in the perturbation scheme. An ordered set of lower bounds is derived for the first of these sums and also for similar expressions for van der Waals force constants. Third, the contribution of each electron is considered separately. The lower bounds are evaluated exactly with the help of the sum rules developed. In this way are obtained for the approximate values of the atomic polarizability of beryllium and argon  $4.14 \times 10^{-24}$  cm<sup>3</sup> and  $1.28 \times 10^{-24}$  cm<sup>3</sup>, respectively. Likewise the constant  $\mu$  in the van der Waals energy,  $-\mu/R^6$ , is found to be about  $222 \times 10^{-60}$  erg cm<sup>6</sup> for two beryllium atoms and  $63.7 \times 10^{-60}$  erg cm<sup>6</sup> for two argon atoms. The observed atomic polarizability of argon is  $1.63 \times 10^{-24}$  cm<sup>3</sup>.

### SUM RULES FOR THE FOCK EQUATION

IN the Hartree-Fock method<sup>1</sup> of dealing with the Schrödinger equation there is assigned to a state of the system an approximate wave function having the proper symmetry and made up of products of single-particle functions. For an atom with  $N$  electrons in a nondegenerate state, the approximate wave function has the form

$$\Phi(A) = \mathcal{Q}u_1(a^1)u_2(a^2) \cdots u_N(a^N). \quad (1)$$

$A$  stands for the collection of quantum symbols  $a^1, a^2, \dots, a^N$ ; the functions  $u(a)$  are orthogonal normalized functions of the space and spin coordinates,  $xyz\sigma$ , of a single electron; and  $\mathcal{Q}$  is the normalized antisymmetrizing operator.<sup>2</sup>

\* On leave from Purdue University, 1937-38.

<sup>1</sup> D. R. Hartree, Proc. Camb. Phil. Soc. 24, 89 (1928); V. Fock, Zeits. f. Physik 61, 126 (1930); P. A. M. Dirac, Proc. Camb. Phil. Soc. 26, 376 (1930).

<sup>2</sup>  $\mathcal{Q} = [N!]^{-1/2} \sum_p (-)^p P$ , where  $P$  is a permutation of parity  $p$  of both positional and spin coordinates of the electrons. The notation of this paper follows more or less that of Condon and Shortley, *Theory of Atomic Spectra*. It

For the purpose of Hartree-Fock calculations the atomic Hamiltonian is assumed to be

$$H = \sum_{i=1}^N H_i^0 + Q; \quad (2)$$

$$H_i^0 = (1/2m)p_i^2 - Ze^2/r_i,$$

$$Q = \frac{1}{2} \sum_{i \neq j} q_{ij}, \quad q_{ij} = e^2/r_{ij}.$$

In terms of the two expressions

$$\langle a | H^0 | a \rangle = \sum_{\sigma} \int d\tau u^*(a) H^0 u(a), \quad (3)$$

$$\langle ab | q | cd \rangle = \sum_{\sigma_1 \sigma_2} \int d\tau_1 \int d\tau_2 u_1^*(a) u_2^*(b) \times q_{12} u_1(c) u_2(d),$$

is an adaptation of the general Dirac notation to atomic problems. Coordinates are usually indicated through subscripts which indicate the particles to which functions belong. Quantum symbols appear in the main line of print.