PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Equilibrium and Non-Equilibrium Electrical Conductivity of Seeded Combustion Products

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Phil. Trans. R. Soc. Lond. A 1967 **261**, 471-485
doi: 10.1098/rsta.1967.0015

XI. Equilibrium and non-equilibrium electrical conductivity of seeded combustion products

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From measurements by four electrode and microwave techniques and from theoretical calculations, the conclusions are drawn that the equilibrium electrical conductivity varies with fuel/air ratio, being higher in fuel rich conditions, and that the chlorine and sulphur impurities in power station fuels will not significantly affect the conductivity under m.h.d. generator conditions.

Experiments on non-equilibrium conductivity in seeded combustion products at 1500 °K are described. The form of the current-field curve at high values of the ratio of electrical field to molecule density was investigated. At a certain value of the field the current was found to increase many times above the equilibrium value, with little increase in field.

To describe these results, a theory is presented in which ionization by electrons having energies greater than the ionization potential is balanced by a three-body recombination process involving electrons, positive potassium ions, and neutral molecules. This gives a current-field curve of the same shape as that experimentally observed but the experimental value of the field at which the current rises differs from the theoretical value by about 25%.

The use of this non-equilibrium conductivity in generators is discussed.

1. Introduction

The output power W of an m.h.d. generator per unit volume of duct space is given by

$$W = \sigma v^2 B^2 K(1-K),$$

where σ is the conductivity of the working fluid, v is the velocity of the working fluid, B is the magnetic flux density and K is a dimensionless parameter, varying between 0 and 1, which denotes the loading of the generator. The value of the conductivity affects, in the first instance, the size of the generator and, consequently, the amount of capital required for the duct and magnet. However, the conductivity can also effectively determine the useful efficiency. For a given cost per kilowatt-hour there is a relation between capital cost, load factor, the return required on capital, efficiency and fuel costs. If the conductivity at a point along the generator falls below a certain value, the extra power output obtained after this point will not be worth the extra capital expended in providing the larger duct and magnet. An example of this is the rapid fall of thermal equilibrium conductivity with fall in temperature, which sets a lower limit to the useful exit temperature and, if the highest temperature of the air preheater is considered fixed, a limit to the useful efficiency of the m.h.d. section of a station.

2. Thermal equilibrium conductivity

(a) *Pure combustion products*

The conductivity is given by $\sigma = n_e e \mu$,

where n_e is the electron density, e the electronic charge and μ the mobility.

In thermal equilibrium at a temperature T °K the ionization of the potassium seed is given by the Saha equation

$$\frac{n_e n_i}{n_0} = 2\frac{g_i}{g_0}\frac{(2\pi m\,kT)^{\frac{3}{2}}}{h^3}\exp\left(-\frac{eV_i}{kT}\right),$$

where n_i and n_0 are the densities of potassium ions and neutral potassium atoms respectively. The ratio g_i/g_0 of the statistical weights of the ion and the neutral atom is $\frac{1}{2}$ for the alkali metals. V_i, the ionization potential, is 4·34 eV. However, in combustion products, the chemical combination of the potassium atoms with other species reduces the amount of potassium available for ionization and has to be taken into account. Another factor is the attachment of electrons to electronegative species in the combustion products. This reduces the density of electrons given by a certain quantity of free potassium atoms.

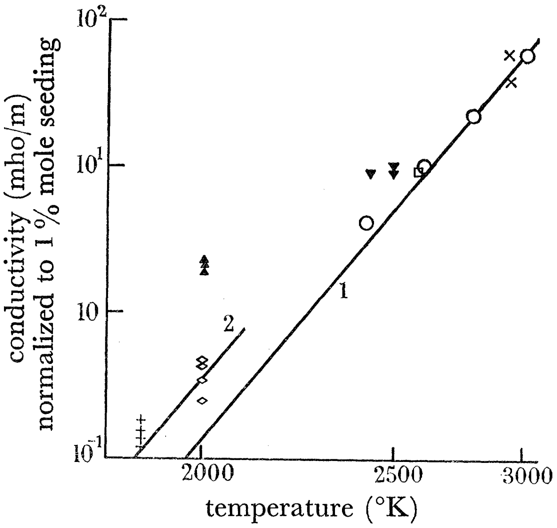

FIGURE 1. Results of different workers in conductivity experiments. Combustion in oxygen: ×, Brogan Kantrowitz, Rosa & Stekly (1961); ○, Brogan (1962); ▽, Jones & McKinnon (1962); □, Jones *et al.* (1963); △, Mullaney *et al.* (1961); ◇, Zimin & Papov (1962); curve 1, theoretical. Combustion in air; +, present work; curve 2, theoretical.

Frost (1961), in calculating the electron density in the combustion products of a pure hydrocarbon fuel in oxygen, took into account the formation of potassium hydroxide, for which he estimated the value of the equilibrium constant, and the formation of negative hydroxyl ions. His calculation of the effect of hydroxyl ion formation was performed for two values of the electron affinity of hydroxyl, 2·1 and 2·65 eV, owing to the uncertainty of the experimental information on this parameter. Way, Young, Tuba & Chambers (1965) have suggested that in the products of combustion in air electron attachment to nitrogen dioxide should also be considered.

Figure 1 shows several workers' conductivity measurements, normalized to 1 % mole seeding and compared with theoretical lines. The theoretical line for combustion in oxygen was taken from Frost (1961). The theoretical line for combustion in air was taken from Freck (1964), who used the same basic data and method of calculation as Frost (1961). In the calculation of both theoretical lines the 2·1 eV value of the hydroxyl electron affinity was used. It can be seen that, for combustion in oxygen, the results agree well with theory at the higher temperatures at which the effect of potassium hydroxide and hydroxyl ion formation is small. This agreement between theory and experiment therefore indicates that the mobility calculation is not seriously in error and that the Saha equation is followed. At the lower temperatures, the experimental results for both combustion in oxygen and combustion in air tend to be higher than their respective theoretical lines. Since the mobility values are not likely to be as much in error as this implies, while providing good agreement at the higher temperatures the results indicate that the theoretical calculations overestimate the amount of potassium hydroxide or hydroxyl ion formation. With the chosen value of the hydroxyl electron affinity of 2·1 eV the effect of hydroxyl ion formation is small compared with the effect of potassium hydroxide formation so that even if there were no electron attachment the discrepancy would be unaccounted for. Although this points to a change in the equilibrium constant for the formation of KOH the JANAF (1962) table gives a value which is quite close to Frost's value and moreover would give a conductivity a few per cent lower than the theoretical values given here. In view of the fact that the experimental results tend to be higher than the theoretical values it is unlikely that negative nitrogen dioxide ions can be formed in the quantities suggested by Way *et al.* (1965) since this would result in the reduction of the conductivity by about a factor of 2. A value of the electron affinity of nitrogen dioxide of 3·6 eV formed the basis of their suggestion but it would require only a small error in this value, say, a change to 3·3 eV to make the effect of nitrogen dioxide ions negligible. The high values of conductivity obtained by Mullaney, Kydd & Dibelius (1961) may have been due to the very fuel-rich nature of the combustion products and the presence of large amounts of burning carbon in their experiments. The conclusion may be drawn from the foregoing discussion that if Frost's method of calculating conductivities in the combustion products of pure hydrocarbon fuels is adopted with a value of 2·1 eV for the electron affinity of the hydroxyl radical the values obtained will be satisfactory for high temperatures but some 30% to 40% too low at low temperatures.

Freck (1964) showed that, consequent upon the variation with fuel/air mixture ratio of the amount of potassium hydroxide formed, the conductivity should vary with mixture ratio, being higher in fuel rich conditions. Experimental measurements on pure hydrocarbon air combustion products by a four electrode technique and a microwave technique are shown in figures 2 and 3 respectively. The seed was introduced as potassium octoate.

These measurements show higher conductivities in the fuel-rich region but in the microwave measurements the conductivity begins to fall again at very fuel-rich mixtures. This last point is not understood. The theoretical lines are taken from Freck (1964) using Frost's value of the potassium hydroxide equilibrium constant. The errors in measuring conductivity are high because of the very rapid variation of conductivity with temperature, a $1\frac{1}{2}\%$ error in measuring temperature at 1900 °K giving a 30% error in measuring conductivity.

A consequence of the formation of potassium hydroxide and hydroxyl ions is that the variation with pressure P of the electron density changes from the $P^{\frac{1}{2}}$ law (which would be expected if no potassium hydroxide or hydroxyl ion formation took place) at high temperatures to a $P^{-\frac{1}{2}}$ law at low temperatures. Taken with the P^{-1} variation of mobility with pressure this gives a $P^{-\frac{1}{2}}$ law for conductivity at high temperatures changing to a $P^{-\frac{3}{2}}$ law for conductivity at low temperatures.

(*b*) *Effects of impurities*

A factor that has to be considered in a power station m.h.d. generator is the impurities in the fuels normally used for electricity generation. Sulphur is found to the extent of 4 % by weight in residual fuel oils and to about 2 % in coal.

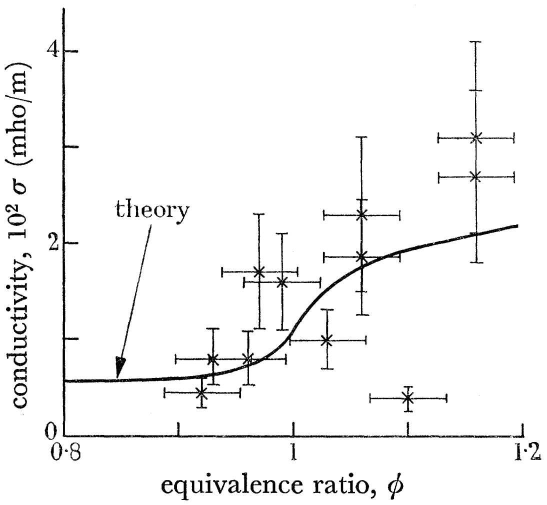

FIGURE 2. Four electrode measurements of electrical conductivity; seeding 0·25 % by weight in the fuel; T = 1870 °K; ϕ defined by $\phi = (\text{fuel/air})/(\text{fuel/air})_{\text{stoich.}}$

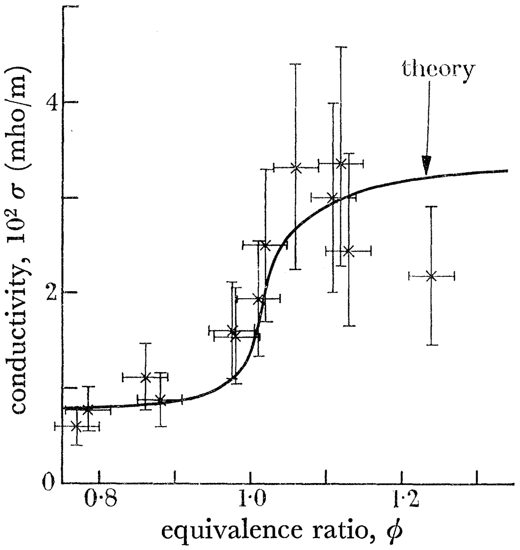

FIGURE 3. Microwave measurements of electrical conductivity; seeding 0·72 % by weight in the fuel; T = 1870 °K.

(i) *Sulphur*

Page (1958) made measurements with hydrogen flames containing sulphur which led him to the conclusion that HS was the most important electronegative radical in these flames. Calculations based on Page's value for the electron affinity of HS indicated that the effect on conductivity in m.h.d. generator conditions should be negligible. The compound containing potassium and sulphur which was thought most likely to form was potassium sulphate. Although theoretical calculations showed that this too ought to have a negligible effect under m.h.d. generating conditions, it was thought desirable to check these points experimentally and to check whether any attachment occurred to a radical containing carbon. Experimental measurements at 1870 °K were made using microwaves. These showed no significant change in conductivity on increasing the amount of sulphur from 0 to 4 % by weight in the fuel. The seeding in these experiments was only 0·25 % potassium by weight in the fuel. From these experiments it was judged that in power station m.h.d. generators where the seed level would be much higher, up to 20 % by weight in the fuel, there would again be no effect due to sulphur.

(ii) *Chlorine*

Chlorine, although a small constituent of residual fuel oils, can be present to the extent of 1 % or more in coals. At first sight, it might seem that chlorine, with its electron affinity of 3·7 eV, would attach most of the free electrons and reduce the electron density by a very large factor. However, an equilibrium analysis was performed taking account of the formation of potassium chloride and hydrogen chloride. This predicted that, if the potassium concentration was much greater than the chlorine, the reduction in electron density would be negligible, there being little free chlorine due to the formation of potassium chloride. As the chlorine concentration became comparable with the potassium concentration the electron density would fall but when the chlorine concentration exceeded that of potassium the amount of free chlorine would be held in check by the formation of hydrogen chloride, and the electron density would level out at a new value.

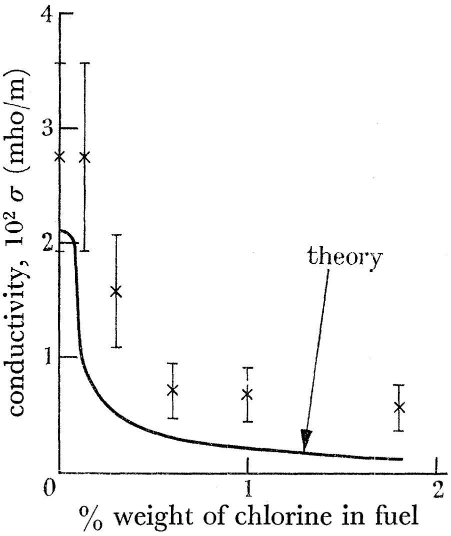

FIGURE 4. Effect of chlorine on conductivity; seeding 0·37 % by weight in the fuel; $\phi = 1{\cdot}05$; $T = 1870$ °K.

Figure 4 shows some microwave measurements of conductivity as a function of chlorine concentration. The potassium concentration was very low, 0·37 % by weight in the fuel. The theoretical curve shown in figure 4 was calculated by considering an equilibrium of potassium, potassium ions, electrons, potassium chloride, potassium hydroxide, hydroxyl ions and chlorine ions. The equilibrium constants for potassium chloride were taken from the JANAF tables, for chlorine ions and hydrogen chloride from Mullaney & Dibelius (1963), and for hydroxyl ions (2·1 eV electron affinity), potassium hydroxide, and the ionization of potassium, from Frost (1961). The shape of the theoretical curve follows the experimental results but predicts lower actual values than the experimental points.

From the theory and the experiments it can be said that in m.h.d. power station generators, where the seed concentration is likely to be some 20 % by weight in the fuel, chlorine concentrations up to 2 % by weight in the fuel would produce negligible reductions in conductivity. If the seed concentration were reduced so that the chlorine concentration became comparable with that of the seed, a considerable reduction in conductivity would be expected.

3. NON-EQUILIBRIUM CONDUCTIVITY

Because of the rapid fall of thermal equilibrium conductivity with temperature which limits the efficiency of generators using it, a non-equilibrium conductivity which does not primarily depend on temperature is of great interest. In the rest of this paper experiments on seeded combustion products at high values of the ratio, E/N, of electric field, E, to molecule density, N, will be described. A theory to explain the results will be given, and the possible application of the observed phenomena to generators will be discussed.

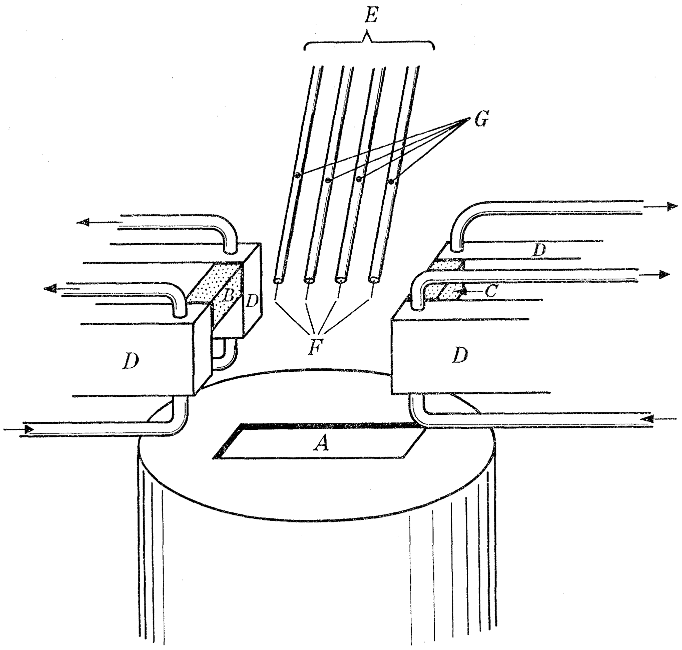

FIGURE 5. Experimental apparatus for non-equilibrium conductivity measurements.

(a) *Experimental measurements*

Figure 5 shows a view of the essential part of the apparatus used. Combustion products of kerosene and air, seeded by dissolving potassium octoate in the kerosene, were emitted from the rectangular orifice *A*. This orifice had dimensions of 5 and 3 cm, giving a gas velocity, at the orifice, of 40 m/s. The temperature of the gas issuing from the orifice was 1500 °K, measured by the sodium *D* line reversal technique.

The electrical conductivity of the combustion products under the influence of high electric fields was measured by the electrode assembly immersed in the rectangular jet of combustion products. The electrode assembly consisted of two hot carbon electrodes *B* and *C* serving as anode and cathode respectively. The electrodes were 3 cm long with a square cross-section of 1 cm side. They were heated by being clamped between heavy watercooled copper bars *D*, with a low voltage, high current, a.c. supply across each pair of copper bars. In all of the experiments the cathode was heated to at least 2800 °K by passing a current of about 1200 A, and the anode was heated to at least 2500 °K by passing a current of about 1000 A.

The potential at four points between the two carbon electrodes was measured by means of four probes *E*. Each probe consisted of a tungsten rod *F*, 1 mm in diameter, projecting about 1 cm from an insulating alumina tube *G* with an outside diameter of 2 mm. The carbon electrodes would only last for about 2 min with the heating current on, so that they were usually renewed before each experiment. The probes, in general, lasted for a much longer time and only had to be renewed after about half an hour in the flame.

All the potentials of probes and electrodes were recorded simultaneously together with the current on a u.v. recorder. A voltage was applied to the two carbon electrodes from a 2 kV 1 A d.c. supply through a ballast resistor of approximately 500 ohms.

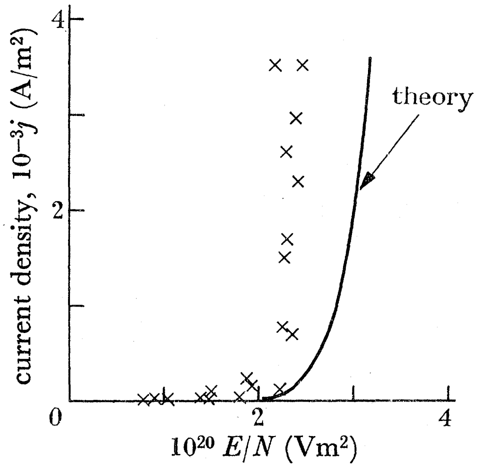

FIGURE 6. Theory and experiment; current density–field characteristics: seeding $1{\cdot}2 \times 10^{-4}$ mole in gases; $T = 1500$ °K.

Figure 6 shows the experimentally observed variation of the current with the average field *E* between the carbon electrodes. This average field was obtained merely by dividing the voltage difference between the two electrodes by the distance between them. In order to compare the experimental results with the theory to be given later, the axes of figure 6 are current density *j* in amperes/metre^2 and E/N in volts metre^2. The molecule density *N* was corrected, at the higher values of *j*, for the Joule heating of the gas. In converting the experimentally observed values of current to current densities the assumption was made that the currents flowed uniformly over an area of 2 cm^2 (the heated length of each carbon electrode was about 2 cm). The expected equilibrium current density at a value of E/N of 2×10^{-20} V m^2 is 2×10^1 A/m^2. Up to a value of E/N of $1{\cdot}4 \times 10^{-20}$ V m^2 the current is approximately the equilibrium current though it is not accurately measured at this low level, in this experiment. Above the value of E/N of $1{\cdot}4 \times 10^{-20}$ V m^2 the current rises more and more steeply until at a value of E/N of about $2{\cdot}3 \times 10^{-20}$ V m^2 the current rises without further increase in E/N.

The composition of the combustion products in figure 6 was $CO_2 + H_2O + 5{\cdot}64N_2$ with a potassium seeding of $1{\cdot}2 \times 10^{-4}$ mole in the gases. The experiment was repeated with different compositions of combustion products and different seedings. By burning a mixture of carbon monoxide and kerosene in air the composition was altered to

$$2{\cdot}3CO_2 + 3H_2O + 5{\cdot}64N_2,$$

simulating coke combustion products with again a potassium seeding of $1{\cdot}2 \times 10^{-4}$ mole. This change made no significant alteration to the current–field characteristic observed.

Burning kerosene in an atmosphere of argon and oxygen changed the composition to $CO_2 + H_2O + 7{\cdot}50\,Ar$ again with $1{\cdot}2 \times 10^{-4}$ mole seeding. This reduced the value of E/N at which the current rose without increase in field by a factor of 2·3. Kerosene–air combustion products of $CO_2 + H_2O + 5{\cdot}64N_2$ composition were tried with $9{\cdot}6 \times 10^{-4}$ mole potassium seeding and with $1{\cdot}2 \times 10^{-4}$ caesium seeding. Both these changes reduced the value of E/N at which the current rose without increase in field by about 20 % from that observed with $1{\cdot}2 \times 10^{-4}$ mole potassium seeding.

(*b*) *Theory of non-equilibrium ionization and recombination*

(i) *Electron energy distribution*

The theoretical approach used by Kerrebrock (1961, 1964) to describe non-equilibrium conduction in seeded monatomic gases cannot be applied to combustion products under most of the conditions of interest. This is because the electron energy distribution in combustion products under non-equilibrium conduction conditions is very different from a Maxwellian distribution. Kerrebrock (1964) has used the inequality $n_e^2 S_c \gg \lambda n_e n_0 S_0$ as a criterion to be satisfied in order that the electrons shall have a Maxwellian distribution. (S_c is the coulomb collision cross-section, λ is the fractional energy loss of an electron upon collision with a neutral molecule and S_0 is the electron collision cross section of neutral molecules.) Kerrebrock's criterion is just a statement that the interchange of energy between electrons themselves shall be greater than the interchange of energy between electrons, the electric field, and neutral molecules. This allows the electrons to be a separate assembly with a Maxwellian distribution of energies and described by a definite temperature. The criterion reduces to

$$\frac{n_e}{n_0} \gg \frac{\lambda S_0}{S_c},$$

S_c is 1×10^{-17} m^2 (10^{-13} cm^2). For seeded monatomic gases $\lambda = 10^{-4}$ and S_0 is 1×10^{-19} m^2 (1×10^{-15} cm^2). For a gas at 1500 °K and 1 atm n_0 is 5×10^{24} m^{-3}. Thus with seeded monatomic gases under these conditions the criterion is satisfied for electron densities greater than 5×10^{18} m^{-3}. However, with seeded combustion products λ is 5×10^{-2}, S_0 is 3×10^{-19} m^2 (3×10^{-15} cm^2) and the criterion is only satisfied at 1 atm by electron densities greater than $7{\cdot}5 \times 10^{21}$ m^{-3}.

Hence the first problem in the theory of non-equilibrium conduction in combustion products is to calculate the electron energy distribution as a function of applied field. To do this exactly, involves solving the Boltzmann equation, including elastic collisions, inelastic collisions, electron–ion collisions and electron–electron collisions, for the mixture of gases, that is, combustion products. This formidable task has not yet been performed. Engelhardt, Phelps & Risk (1964) have numerically solved the Boltzmann equation, including elastic and inelastic collisions, for electrons in pure nitrogen, for various values of the ratio E/N. They publish in their paper the electron energy distributions for three values of E/N. Carleton & Megill (1962) in a similar computation publish electron energy distributions for electrons in upper altitude air for five values of E/N. The effect of nitrogen, 60 % by volume of the chosen composition, was found to be dominant in Carleton & Megill's work. In both Carleton & Megill's work and that of Engelhardt *et al.* the effect of electron–electron collisions was not included.

In the present work, in order to be able to construct an approximate theory quickly, the existing electron energy distributions for nitrogen of Engelhardt *et al.* and Carleton & Megill were used without alteration. This involved the neglect of the difference between the cross sections of nitrogen and the minor constituents, carbon dioxide and water vapour. The negligible change in the current–field characteristic on changing the composition from $CO_2+H_2O+5{\cdot}64N_2$ to $2{\cdot}3CO_2+0{\cdot}3H_2O+5{\cdot}64N_2$ is some slight support for this assumption. The influence of electron collisions with seed atoms on the electron energy distribution was also neglected. This involves an error which becomes appreciable if the seed concentration exceeds 1 % mole. Further, electron–electron collisions, which are most important at high electron densities, were also neglected. The electron energy distributions used are shown in figure 7 as a function of E/N. In calculating N for the upper altitude air of Carleton & Megill's paper, only the nitrogen molecules were counted since the other molecules of O_2 and O had a very small effect, as demonstrated in their paper. It was thought that neglecting the O_2 and O molecules would be a better approximation than counting them as nitrogen molecules. $f(\epsilon)\,\mathrm{d}\epsilon$ in figure 7 is the fraction of electrons having energies between ϵ and $\epsilon+\mathrm{d}\epsilon$. Also shown for comparison in figure 7 are Maxwellian and Druyvesteyn distributions with a mean energy of 0·77 eV. It should be noted how different is the population at high energies, say 4 eV, in these distributions, from the high energy population of the actual computed distribution, curve *B*, with a mean energy of 0·77 eV. It should also be noted how rapidly the population at high energies varies as a function of E/N. In using the distributions of figure 7 in the present work any effect of differences of gas temperature other than on number density of molecules was ignored; the gas temperature in the work of Engelhardt *et al.* was 77 °K; the temperature in the present experiments

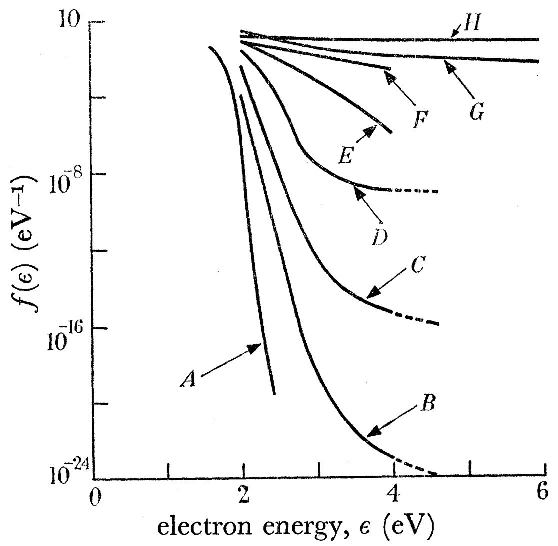

FIGURE 7. Electron energy distribution. Carleton & Megill (1962); *A*, $E/N = 2{\cdot}5\times10^{-21}$ Vm^2, mean energy = 0·56 eV; *B*, $E/N = 5{\cdot}0\times10^{-21}$ Vm^2, mean energy = 0·77 eV; *C*, $E/N = 7{\cdot}5\times10^{-21}$ Vm^2, mean energy = 0·87 eV; *D*, $E/N = 1{\cdot}25\times10^{-20}$ Vm^2, mean energy = 0·95 eV. Druyvesteyn; *E*, mean energy = 0·77 eV. Maxwellian; *F*, mean energy = 0·77 eV. Engelhardt *et al.* (1964); *G*, $E/N = 6\times10^{-20}$ Vm^2, mean energy = 1·5 eV. *H*, $E/N = 3\times10^{-19}$ Vm^2, mean energy = 4·6 eV.

was 1500 °K. The principal effect of this is to underestimate the effect of superelastic collisions. However, the effect of superelastic collisions on the population at high electron energies, which is of most interest here, is likely to be very small. Carleton & Megill's work itself neglects superelastic collisions completely.

From the electron energy distributions shown in figure 7 (extrapolating Carleton & Megill's curves above 4 eV where necessary) the total fraction F of electrons having energies above the ionization potential, ϵ_I (K), of potassium (4·34 eV) and above the ionization potential, ϵ_I (Cs), of caesium (3·89 eV) can be calculated for different values of E/N by estimating the area under the distributions for energies greater than the ionization energy,

$$F(\mathrm{K}) = \int_{\epsilon_I(\mathrm{K})}^{\infty} f(\epsilon)\,\mathrm{d}\epsilon,$$

$$F(\mathrm{Cs}) = \int_{\epsilon_I(\mathrm{Cs})}^{\infty} f(\epsilon)\,\mathrm{d}\epsilon.$$

Values of F(K) and F(Cs) for different values of E/N are shown in table 1 and F(K) is plotted with a smooth curve drawn between the points in figure 8.

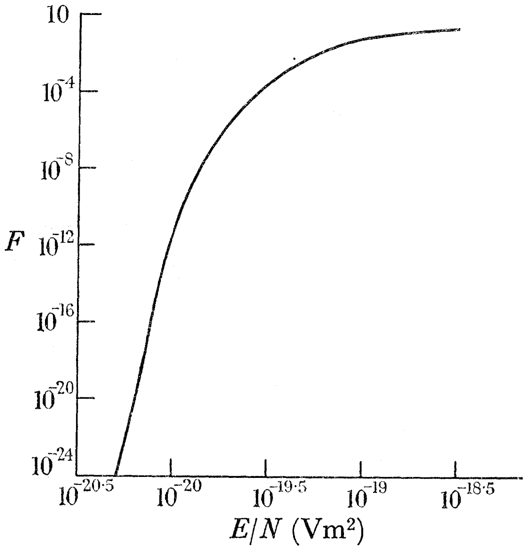

Figure 8. Fraction of electrons with energies greater than 4·34 eV.

Table 1. Fraction of electrons having energies above the ionization potential

curve (fig. 7)	E/N (Vm^2)	$f(\epsilon_I(K))$ (eV^{-1})	estimate F (K)	$f(\epsilon_I(\mathrm{Cs}))$ (eV^{-1})	estimate F (Cs)
A	2.5×10^{-21}	$\ll 10^{-24}$	$\ll 10^{-24}$	$\ll 10^{-24}$	$\ll 10^{-24}$
B	5.0×10^{-21}	10^{-24}	2×10^{-25}	10^{-23}	2×10^{-24}
C	7.5×10^{-21}	3×10^{-16}	3×10^{-17}	10^{-15}	10^{-16}
D	1.25×10^{-20}	10^{-9}	10^{-9}	10^{-9}	10^{-9}
G	6×10^{-20}	1×10^{-2}	1.5×10^{-2}	1.2×10^{-2}	1.8×10^{-2}
H	3×10^{-19}	7×10^{-2}	2.8×10^{-1}	8×10^{-2}	3.2×10^{-1}

Note that the curve of Engelhardt *et al.* for the value of E/N of 1×10^{-20} V m^2 is not used because extrapolation would be too inaccurate.

(ii) *Rate of ionization*

Let c be the fraction of atoms that are potassium atoms and S_i the cross-section for ionization of potassium by electrons with energies greater than $\epsilon_I(\mathrm{K})$. Then

$$N = 4{\cdot}89\times 10^{24}\,P/1\;(1500/T)/\mathrm{m}^3\;(N = 4{\cdot}89\times 10^{24}/\mathrm{m}^3 \text{ at}$$

$$P = 1\text{ atm} \quad\text{and}\quad T = 1500\,^\circ\mathrm{K}).$$

Density of potassium atoms $= 4{\cdot}89\times 10^{24}\,P/1\;(1500/T)\,c/\mathrm{m}^3$; velocity of 4·5 eV electron $= 1{\cdot}26\times 10^6$ m/s; density of electrons with energies greater than $\epsilon_I(\mathrm{K}) = F(\mathrm{K})n_e$.

Hence, number of ionizations of potassium atoms per second

$$= F(\mathrm{K})n_e\;1{\cdot}26\times 10^6\;S_iNc. \tag{1}$$

The values of S_i given in the literature (Funk 1930; Tate & Smith 1934; Kaneko 1961; Brink 1962; Fiquet & Fayard 1963; McFarland & Kiney 1964) differ somewhat. There is also a sharp variation of S_i with electron energy above the ionization energy. In order to be able to use a simple single value of S_i a mean figure of 10^{-20} m^2 (10^{-16} cm^2) was arbitrarily chosen. In calculating the value of c the formation of potassium hydroxide was taken into account.

(iii) *Recombination rate*

Recombination rates have been reviewed by McNab & Robinson (1962). Of the recombination processes listed by them the most likely, under the conditions considered in the present paper, is a three-body process involving an electron, a positive potassium ion and a neutral molecule. This neutral molecule removes the excess energy in its vibrational or rotational states. McNab & Robinson (1962) suggest the following formula for the recombination coefficient:

$$\alpha = \frac{3{\cdot}6\times 10^{-11}\,n_0\lambda S_0}{T_e^{\frac{5}{2}}}; \tag{2}$$

α is the usual recombination coefficient defined by

$$\alpha = -\frac{\mathrm{d}n_e}{\mathrm{d}t}\,\frac{1}{n_e^2}. \tag{3}$$

This formula is based on that given by Massey & Burhop (1952) who applied Thomson's (1924) recombination theory to this particular case. T_e is the electron temperature. The formula cannot be applied exactly to the situation where the electron energy distribution is non-Maxwellian. However, the electron energy distributions in the present paper differ from a Maxwellian distribution most markedly in the high energy tail upon which recombination, unlike ionization, does not depend. The Maxwellian formula therefore describes recombination adequately and equation (2) was used with

$$T_e = \tfrac{2}{3}(\bar{\epsilon}/k),$$

where $\bar{\epsilon}$ is the mean electron energy and k is Boltzmann's constant. For the various gases in combustion products, values of λ and S_0 were taken from Healey & Reed (1941) and Frost (1961) respectively.

(iv) *Steady state electron density*

The steady state electron density for a given value of E/N is obtained by equating the rates of ionization and recombination calculated in previous sections. Hence we have

$$F(\mathrm{K})\, n_e\, 1{\cdot}26 \times 10^6\, NcS_i = \alpha n_e^2.$$

This reduces to

$$n_e = \frac{F(\mathrm{K})\, cS_i\, 1{\cdot}26 \times 10^6 N}{\alpha}. \tag{4}$$

$F(\mathrm{K})$ for a particular E/N is to be obtained from figure 8.

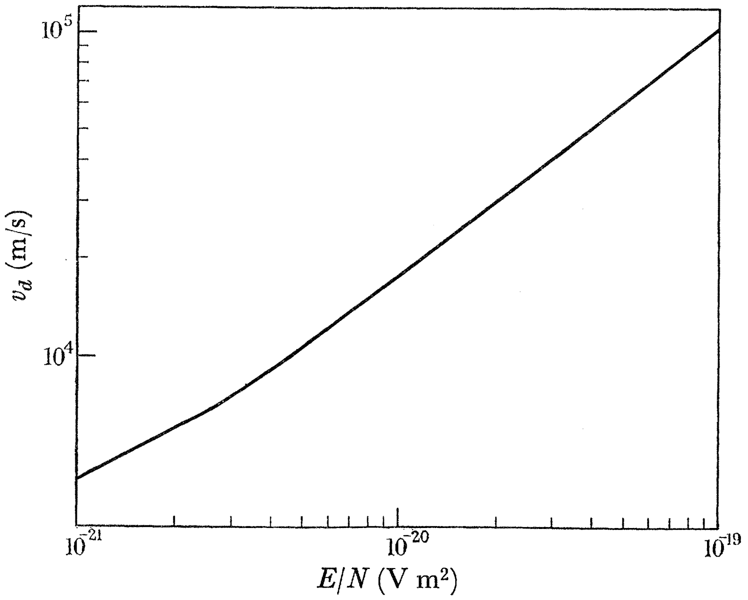

FIGURE 9. Drift velocity plotted against E/N.

TABLE 2

constituent	fraction	$10^{-14}\,\nu_c$ at 1 eV $(\mathrm{s^{-1}\,m^3})$		ν_c at 1 eV $(\mathrm{s^{-1}})$
N_2	$\simeq \frac{3}{4}$	12ϵ	12	$4{\cdot}4 \times 10^{11}$
CO_2	$\simeq \frac{1}{8}$	$1{\cdot}7\epsilon^{-\frac{1}{2}} + 2{\cdot}1\epsilon^{\frac{1}{2}}$	3·8	$2{\cdot}3 \times 10^{10}$
H_2O	$\simeq \frac{1}{8}$	$10\epsilon^{-\frac{1}{2}}$	10	$6{\cdot}1 \times 10^{10}$
K	1 %	160	160	$7{\cdot}8 \times 10^{10}$
	0·01 %			$7{\cdot}8 \times 10^{8}$

(v) *Electrical conductivity: the variation of j with E/N*

$$j = n_e e v_d, \tag{5}$$

where v_d is the drift velocity of the electrons.

Engelhardt *et al.* (1964) give values of v_d as a function of E/N. Their values, which are for pure nitrogen, are shown in figure 9. Table 2 shows the electron collision frequencies $\nu_c(v_{da}/\nu_c)$ with the main constituents of combustion products at 1 eV electron energy, which is the region of interest in the present work. The formulae given by Frost (1961) were used to compile table 2.

From table 2 it can be seen that the presence of CO_2 in the combustion products might raise the drift velocity slightly as compared with pure nitrogen. However, this was neglected and the drift velocities were taken directly from figure 9.

Thus in order to calculate j for any E/N, n_e was obtained from equation (4), vd from figure 9 and j from equation (5). Figure 6 shows the resultant curve of j versus E/N for the same conditions of temperature and pressure as the experimental points on figure 6.

(c) *Discussion of non-equilibrium theory and experiments*

The theory and experimental results are compared in figure 6. The theoretical curve has the same shape as the curve of the experimental results but, experimentally, the field at which the current rises, with very little increase in field, differs from the theoretical value by about 25%.

If the parameters cS_i/α in equation (4) were changed by a factor of 16 the theoretical curve would fit the experimental points quite well. Such a large change in cS_1/α produces only a small change in the field at which the current rises because of the shape of the curve in figure 8. It is quite conceivable that, because of the approximations used in the theory and the uncertainties in the values of the basic parameters, such as S_1 and α, there could be an uncertainty of this size in the theory. However, it is more likely that the experimental value of the field at which the current rises is in error. The separation between the two carbon electrodes was normally only about 15 mm and preliminary measurements with the voltage probes indicated that the field was low for a distance of about 2 to 3 mm from the cathode. This was probably due to excess emission from the very hot cathode. Further, more accurate, experiments using voltage probes and wider electrode spacings are required before the present theory should be regarded as at variance with experiment. The present theory and experiment represent only the first, relatively crude, exploration of a new area.

One serious objection that can be raised against the present experiments and their theoretical interpretation is that there is no proof that the current flow was uniform. The current might have been flowing in a narrow channel which was heated by Joule heat to a temperature sufficient to carry the current by equilibrium conduction. The flow velocity of the combustion products was of course chosen so that the joule heating due to uniform current flow would not cause appreciable equilibrium conduction. The same objection can be raised to all experiments with applied electric fields in monatomic gases. While it is true that no positive conclusive experiment has been performed to refute this objection there is evidence against it. A search with the sodium D line technique failed to reveal any high temperature narrow channel nor was it visible to the eye. This, of course, is not positive evidence that it did not exist; it may have been moving rapidly from point to point or have been too narrow to be detected. The shape of the current–field characteristic is not typical of an arc, nor are the fields and currents involved. In the experiment in which the nitrogen in the combustion products was replaced by argon, the field at which the current rose dropped by a factor of 2·3. The non-equilibrium theory given in this paper predicts that this factor should be 2·6, in good agreement with the experiment. It would be a coincidence for equilibrium conduction in a narrow channel to give a similar field ratio. One experiment that would verify that the conduction was non-equilibrium would be the finding of electron densities above equilibrium values, downstream of the electrodes.

If the experiments of the present type were extended to higher current densities and lower pressures it might be found that the values of E/N required to maintain the current would be less because electron–electron collisions become more important and the electron energy distribution approaches a Maxwellian one as the ratio n_e/n_a rises.

4. Application of non-equilibrium conductivity in generators

A possible way of utilizing the non-equilibrium phenomena discussed in this paper would be the type of generator in which, after acceleration to a high velocity, say 2×10^3 m/s, and a low static pressure, say 0·1 atm, the gases would have an electric field applied to them to produce non-equilibrium ionization.

Alternative means of production of non-equilibrium ionization could be used, i.e. electron beams or frozen thermal ionization. The gases would then pass into a generating section in which generation would have to take place before the non-equilibrium electrons and ions recombined and the conductivity fell. A key parameter in a system of this kind is the recombination rate. The rate of rise of ionization in the applied electric field is also of importance. It is not very useful to discuss, in detail, the possible performance of a generator of this type while the values of the basic parameters are so uncertain. However, as an indication of the possibilities, if equation (2) is used for the recombination rate, a generator design can be drawn up which gives an m.h.d. generator with a better efficiency than the m.h.d.-steam, combined generator now envisaged, and only employs air preheating to 800 °C. This improvement, of course, occurs because the non-equilibrium conductivity does not fall with temperature as equilibrium conductivity does. Operation at a low static pressure is necessary because the recombination rate falls with fall in electron density and a low pressure gives the best conductivity for a given electron density. If the exit stagnation pressure was below 1 atm, the necessary exhaust compressor would have to be placed after the air preheater so that it worked in cold combustion products.

This mode of producing non-equilibrium ionization is similar to that of Karlovitz & Helasz (1962). However, they used unseeded combustion products whenever they used applied electric fields to induce ionization, so that their positive ions were molecular and they encountered high recombination rates, presumably due to dissociative recombination. Recombination coefficients due to dissociative recombination are of the order of 10^{-12} m^3/s (Biondi & Brown 1949). The recombination coefficient obtained from equation (2) for a temperature of 1500 °K and pressure of 0·1 atm is $2{\cdot}5 \times 10^{-16}$ m^2/s. This is much lower because the ions are atomic and the recombination process a three-body rather than a two-body process. Whilst the present experiments strongly favour the low recombination coefficient given by equation (2) a more direct measurement of the time a non-equilibrium electron density persists is required before generator schemes can be discussed with any confidence.

The author thanks his colleagues, Mr P. B. Barber, Mr C. N. Carter, Dr J. R. Greig, Dr J. A. Nation and Mr D. P. Simpson who helped to perform the experiments. The work was carried out at the Central Electricity Research Laboratories and is published by permission of the Central Electricity Generating Board.

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