ELECTRICAL CONDUCTIVITY OF AIR IN THE PRESENCE OF AN IMPURITY

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Zhurnal prikladnoi mekhaniki i tekhnicheskoi fiziki, No. 1, pp. 76-82, 1965

Electrical processes in air often lead to the formation of a plasma, a mixture of air and some foreign element (e.g., in the case of an electric discharge the material of the electrode). The presence of an impurity can appreciably affect the electrical conductivity of the air (and, accordingly, the parameters of the effect investigated) for the following reasons.

1. If the atomic concentration of the impurity element is more than 0.001%, while the ionization energy is less than 10 eV, there will be an increase in the concentration of electrons in the plasma, and hence an increase in electrical conductivity.

2. If the atomic concentration of the impurity is more than 0.1%, while the collision cross section for electrons and impurity atoms exceeds $15 \cdot 10^{-16}$ cm^2, the presence of an impurity will lead to a decrease in the mean free path of the electrons in the plasma, and hence to a decrease in electrical conductivity.

This paper is concerned with a method of computing the electrical conductivity of air in the temperature range 1000-10 000°K in the presence of an impurity. It is assumed that the gas mixture investigated is in a state of thermal equilibrium. Results are presented for the conductivity cross sections of the principal components of air. For the case where the concentration of the impurity does not exceed 5% a simple approximate method of determining the composition of the plasma is proposed. The correctness of the computations are checked with the aid of experimental data on the parameters of an arc discharge in air.

1. Electrical Conductivity of a Partly Ionized Gas

We shall assume that the following assumptions are valid: 1) the electron velocity distribution is approximately Maxwellian (this is true in the absence of strong electric and magnetic fields and large temperature and particle concentration gradients [1]); 2) local thermal equilibrium prevails in the plasma (for example, this is always true of an arc discharge in air at atmospheric pressure [2, 3]). Then, in the case of a constant electric field, the electrical conductivity of the plasma can be computed from a formula obtained on the basis of an approximate solution of the Boltzmann kinetic equation [4, 5]:

$$\sigma(T) = \frac{\sqrt{\pi} e^2}{\sqrt{8mkT}} \frac{\alpha N_e}{N_i \langle Q_i \rangle + \sum\limits_l N_l \langle Q_l \rangle} \qquad \left(\alpha = \alpha(\gamma), \quad \gamma = \frac{N_i \langle Q_i \rangle}{\sum\limits_l N_l \langle Q_l \rangle}\right) \tag{1.1}$$

where T is the plasma temperature, m and e are the electronic mass and charge, k is Boltzmann's constant, N_e and N_i are the concentrations of electrons and ions, N_l is the concentration of neutral particles of the l-th kind, $\langle Q \rangle$ are the so-called conductivity cross sections for singly charged ions and neutral particles, as given by the formulas

$$\langle Q_i \rangle = \frac{\pi e^4}{(kT)^2} \ln \left[\left(\frac{9}{8\pi} \right)^{-1/3} \frac{kT}{e^2 N_i^{1/3}} \right] \tag{1.2}$$

$$\langle O_l \rangle = \frac{1}{6} \left(\frac{m}{kT} \right)^3 \int\limits_0^\infty q_l(v)\, v^5 \exp\left(-\frac{mv^2}{2kT} \right) dv \tag{1.3}$$

where $q_l(v)$ is the momentum transfer (transport) cross section of a neutral particle of the l-th kind, which depends on the electron velocity v. The quantity α entering into (1.1), which represents electron-electron interaction, is a complex function* of the ratio γ [4]. For practical purposes it is possible to recommend the approximate formula:

$$\alpha(\gamma) = 1.13 + 0.05\gamma e^{-0.02\gamma} \quad \text{for } 30 > \gamma \geqslant 0, \quad \alpha = 1.95 \quad \text{for} \quad \gamma \geqslant 30\;; \tag{1.4}$$

the results of computations based on this formula agree to within 1% with the true dependence $\alpha(\gamma)$.

Formula (1.1) was obtained on the assumption that the current is transported across the plasma only by electrons (the mobility of the ions is almost 100 times less than that of the electrons) and that the chief part in decelerating the

* A. V. Gurevich, Some Problems of the Theory of Propagation of Powerful Radio Waves in Plasma, Doctoral dissertation, Physics Institute AS USSR, Moscow, 1957.

electrons is played by elastic collisions with neutral particles and ions. The latter assumption is reasonable enough below 10 000°K, when the average energy of the electrons (3/2)kT does not exceed 1.3 eV, which is usually considerably below the energy of excitation and ionization of the neutral plasma particles.

If we substitute values of the constants in (1.1) and (1.2) and express n in cm^{-3}, $\langle Q\rangle$ in cm^2, and T in °K, the formulas become:

$$\sigma(T) = 4.52\cdot 10^{-10}\frac{\alpha N_e}{\sqrt{T}}\frac{1}{N_i\langle Q_i\rangle + \sum_l N_l\langle Q_l\rangle}\ \text{ohm}^{-1}\,\text{cm}^{-1}, \qquad (1.5)$$

$$\langle Q_i\rangle = \frac{2.02\cdot 10^{-5}}{T^2}\lg\left(\frac{425T}{N_i^{1/3}}\right)\ \text{cm}^2. \qquad (1.6)$$

Since data on atomic cross sections are usually presented in the form of a function of the electron energy, it is expedient to introduce into (1.3) the variable $\sqrt{{}^1/_2 mv^2} = x\ \text{eV}^{1/2}$ after which we get

$$\langle Q_l\rangle = \frac{2.08\cdot 10^{12}}{T^3}\int_0^\infty q_l(x)\,x^5\exp\left(-\frac{11600x^2}{T}\right)dx\ \text{cm}^2. \qquad (1.7)$$

2. Conductivity Cross Sections for the Principal Components of Air

In the temperature range 1000-10 000°K air with an impurity consists of a mixture of molecules N_2, O_2, NO, atoms N, O, X (where X denotes the impurity element), ions NO^+, N^+, O^+, X^+, and electrons. Other particles (e.g., Ar, CO, N_2^+, O_2^+) are usually also present, but in view of their low concentration they have practically no effect on the conductivity and may be neglected.

The conductivity cross section for all forms of singly charged ions is the same and may be found from (1.6), provided only that the total concentration of ions in the plasma is known. In order to compute the $\langle Q\rangle$ of the neutral particles, it is necessary to have data on the corresponding momentum transfer cross sections q in the range of electron energies from 0.1 to 10 eV. At lower and higher energies the value of q does not affect $\langle Q\rangle$ in the interval 1000-10 000°K, since at these energies the integrand in (7) is practically zero. Unfortunately, we still lack sufficient data on q for the principal components of air. However, we do have information on the total cross section for collision between an electron and a neutral particle (from Ramsauer measurements) or the total cross section for elastic scattering of an electron* (theoretical calculations). Since at low electron energies (the quantity $\langle Q\rangle$ chiefly depends on the value of q at electron energies of less than 3 eV) the total collision cross section practically coincides with the total cross section for elastic scattering [6], while in these cases the latter usually differs from the momentum transfer cross section by not more than 10% [6, 7], in computing $\langle Q\rangle$ it is possible to use data on all three types of cross section. In practically all cases the error due to this approximation will be less than the error in the available values of the cross sections for interaction of an electron with an atom or a molecule. The data used in computing $\langle Q\rangle$ are briefly reviewed below.

1) The N_2 molecule. For an electron energy of 0-1.5 eV we took data on the momentum transfer cross section from [8] and for 1.5-10 eV data on the total collision cross section from [9]. In the region 1.0-1.8 eV the data of [8, 9] are in sufficiently close agreement (discrepancy less than 10%). Moreover, the relative behavior of the q(v) curve from [9] in the region 2.7-10 eV is confirmed by Neynaber's measurements [10].

2) The O_2 molecule. In the interval 0.03-1.5 eV we used the momentum transfer cross section from [8], and in the interval 1.5-10 eV the total collision cross section from [11]. In the region 1.0-1.8 eV the data of [8, 11] agree to within 5%. The relative behavior of the q(v) curve from [11] is confirmed by Neynaber's measurements [12].

3) The NO molecule. In the interval 0.2-1.4 eV we took the momentum transfer cross section from [8], and the interval 1.4-10 eV the total collision cross section from [11]. The data on the cross section for the NO molecule are less reliable than the corresponding data for N_2 and O_2. However, in view of the relatively low NO content of the air (less than 5%) the error in determining $\langle Q\,(\text{NO})\rangle$ has little distorting effect on the conductivity calculations.

4) The N atom. Over the entire interval 0-10 eV we used the total elastic collision cross section computed theoretically by Bauer and Bron (taken from [10]). In the interval 3-10 eV the shape of their curve is in good agreement with Neynaber's experimental curve [10]; however, the theoretical value is about 40% above the experimental. The reason for this is still uncertain.

* The terminology used in this paper corresponds to that of [6].

5) The O atom. Over the entire interval 0-10 eV we used the total elastic collision cross section computed theoretically in [13]. The experimental data for the interval 2.3 -10 eV [2] give a value 30% below the theoretical. The shapes of the theoretical and experimental q(v) curves are more or less the same.

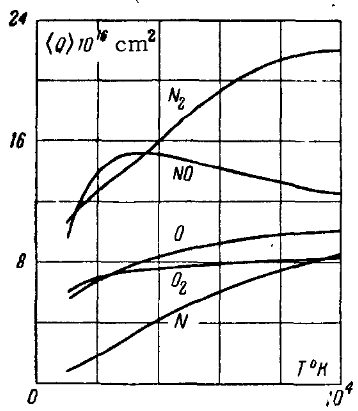

Fig. 1. Conductivity cross sections for the principal components of air.

The results of the computations of conductivity cross sections in the region 1000-10 000°K are presented in Fig. 1. There is no point in extending the computations to include higher temperatures, since at $T > 10^{4\circ}$ K only electron scattering at ions plays an important part, i.e.,

$$N_i\langle Q_i\rangle \gg \sum_l N_e \langle Q_l\rangle .$$

3. Plasma Composition

The particle concentration N can be obtained by solving a system of nonlinear algebraic equations consisting of the Saha equations for the ionization reactions, the equations of the law of mass action (for dissociation reactions), the conditions of quasi-neutrality of the plasma, Dalton's law, and the material balance equations. The numerical method of solving this system was thoroughly investigated in [14, 15] and will not be discussed here. It should be noted, however, that in the cases, commonly encountered in practice, where the concentration of the impurity in the air does not exceed 5%, there is generally no need to perform such a computation, since it is possible to use the available data on the composition of air at different temperatures and pressures [16, 17]. This is done as follows. We put the sum in (1.5) in the form

$$\sum_l N_l \langle Q_l\rangle = A + N(\mathrm{X})\langle Q(\mathrm{X})\rangle \ . \tag{3.1}$$

$$A = N(\mathrm{N_2})\langle Q(\mathrm{N_2})\rangle + N(\mathrm{O_2})\langle Q(\mathrm{O_2})\rangle + N(\mathrm{NO})\langle Q(\mathrm{NO})\rangle + \\ + N(\mathrm{N})\langle Q(\mathrm{N})\rangle + N(\mathrm{O})\langle Q(\mathrm{O})\rangle. \tag{3.2}$$

Since the impurity concentration is low, we can neglect its influence on the concentration of the components of the air and assume that the quantity A(T) is independent of the presence of an impurity. Then, using values of the cross sections $\langle Q\rangle$ (Fig. 1) and data on the composition of air [16, 17], we can calculate A. In order to determine the values of $N_e = N_i$ in (1.5), we can use the following approximate method. The material balance equation representing the ratio of the atomic concentrations of the impurity element and nitrogen has the form

$$\frac{p(\mathrm{X}) + p(\mathrm{X^+})}{2p(\mathrm{N_2}) + p(\mathrm{N}) + p(\mathrm{NO}) + p(\mathrm{N^+}) + p(\mathrm{NO^+})} = a \qquad (p = NkT) \tag{3.3}$$

where p are the partial pressures of the corresponding particles. Neglecting, as before, the influence of the impurity, we can put:

$$2p(\mathrm{N_2}) + p(\mathrm{N}) + p(\mathrm{NO}) + p(\mathrm{N^+}) + p(\mathrm{NO^+}) \approx 2p(\mathrm{N_2}) \cdot p(\mathrm{N}) + p(\mathrm{NO}) = b \ . \tag{3.4}$$

where b(T) is independent of the presence of an impurity. From (3.3) and (3.4)

$$p(\mathrm{X}) + p(\mathrm{X^+}) = ab. \tag{3.5}$$

If we now conditionally assume that electrons are formed in the plasma only at the expense of ionization of impurity atoms, we have

$$p(\mathrm{X^+})\,p(e\mathrm{X}) = K(\mathrm{X})\,p(\mathrm{X}), \tag{3.6}$$

$$p(\mathrm{X^+}) = p(e\mathrm{X}). \tag{3.7}$$

Solving system (3.5)-(3.7), we get:

$$p(e\mathrm{X}) = \sqrt{{}^1/_4 K^2(\mathrm{X}) + K(\mathrm{X})\,ab} - {}^1/_2 K(\mathrm{X}) \tag{3.8}$$

where K(X) is the equilibrium constant of the ionization reaction for the impurity element (numerical values of K for many elements are tabulated in [18]), and p(eX) is the partial pressure of the electrons that would exist in the absence of ionization of the principal components of the air.

Alternatively, if we assume that there is no ionization of impurity atoms, the partial pressure of the electrons in the gas mixture in question will be practically equal to the partial pressure of the electrons p(eO) in air without the impurity (data on p(eO) have been tabulated in [16, 17]).

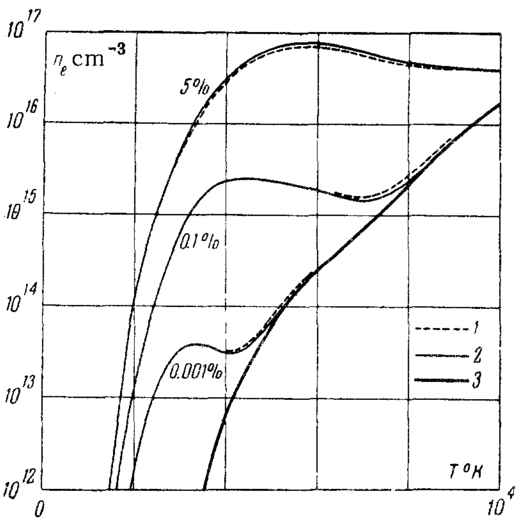

Fig. 2. Electron concentration in air with a cesium impurity: 1) exact calculation, 2) approximate calculation, 3) air without impurity.

Knowing p(eX) and p(eO), we can approximately determine the true electron concentration N_e, without solving the rather complex complete system of equations for the composition of the plasma. Quite satisfactory results are given by the relation:

$$N_e = \frac{p_e}{kT} \approx \frac{1}{kT} \sqrt{p^2(eO) + p^2(eX)}\ , \qquad (3.9)$$

where p_e is the partial pressure of the electrons for simultaneous ionization of the impurity and the components of the air. Figure 2 shows the results of calculating N_e for various concentrations of cesium in air by solving the complete system of equations for the plasma composition (broken-line curve) and by using the approximate method of (3.9) (solid curve). Clearly, at a cesium concentration of less than 1% in temperature intervals where electron formation takes place purely at the expense of ionization of the impurity or, conversely, primarily at the expense of ionization of the components of the air, the two curves coincide. This also follows directly from (3.9), since

$$p_e \approx p(eX) \quad \text{for} \quad p(eX) \gg p(eO)\ ,$$
$$p_e \approx p(eO) \quad \text{for} \quad p(eX) \ll p(eO)\ .$$

The greatest error in calculations based on (3.9) occurs in the case p(eX) ~ p(eO); however, as Fig. 2 shows, it does not exceed 13%. When the Cs concentration is 5%, the value of N_e given by the approximate calculation is too high (by about 10%) over a wide temperature interval, although here the condition p(eX) ≫ p(eO) is fulfilled even better than at lower concentrations of Cs. This exaggeration is due to neglecting the influence of the impurity on the value of b, which becomes appreciable at high concentrations.

The only unknown quantity still needed to compute the electrical conductivity of air with an impurity is the product $N(X)\langle Q(X)\rangle$. In many cases

$$N_i \langle Q_i \rangle + A \gg N(X) \langle Q(X) \rangle\ , \qquad (3.10)$$

and there is no need to determine $N(X)\langle Q(X)\rangle$ But if (3.10) does not hold, N(X) = p(X)/kT can be found from (3.5), (3.6) by substituting p_e for p(eX), and $\langle Q(X)\rangle$ can be calculated in accordance with (1.7) by introducing the corresponding data on the momentum transfer cross section for an impurity atom.

4. Electrical Conductivity of Air with an Impurity at Atmospheric Pressure

For a pressure of 1 atm we calculated the composition of air in the temperature range 1000-10 000°K using the latest data [18] on the equilibrium constants of the ionization and dissociation reactions *, after which we computed the values of A, b, and p(eO) presented in Table 1. With the aid of these values and using the method described above we computed the electrical conductivity of air in the presence of Cs, Na, and Mg (ionization potentials 3.89, 5.14, and 7.64 eV) in concentrations of 0.1 and 1.0%. As Fig. 3 shows, the σ(T) curves have a similar form in each case. At low temperature there is a sharp increase in σ with T, due to ionization of an ever greater number of impurity atoms. Then comes a section where the conductivity depends only slightly on the temperature, since the impurity atoms are almost completely ionized, while electron formation at the expense of the air atoms and molecules is inconsiderable. Finally, at high temperatures the conductivity is relatively independent of the presence of an impurity and approaches that for pure air.

*The results of our calculations agree with the data of [16, 17] to within 1-3%, except that below 7500°K our computed values of the electron concentration are 10-30% higher, due to the difference between the values used for the equilibrium constant of the NO ionization reaction.

Owing to the lack of experimental data, it is only possible to make a rough estimate of the agreement between the calculations and the conductivity of a real plasma. This can be done on the basis of the parameters of an arc discharge in air. For the cross section at the center of the arc the following relation is accurate enough:

$$I = E \int_0^R \sigma(r)\, 2\pi r dr \qquad (4)$$

where I is the current, E is the electric field intensity, r is the distance from the axis of the arc, and R is the distance from the axis at which the conductivity of the plasma becomes quite small (of the order of 1-3% of the maximum value of σ). If we measure E and T(r) for fixed I, then, knowing the concentration of the impurity in the plasma, we can calculate σ(r), and then, with the aid of (4.1), the current I. Then we can judge the correctness of our calculations of the plasma conductivity from the correspondence between the theoretical and the observed values of I.

Table 1

Some Characteristics of Air at Atmospheric pressure

T, °K	A, cm^{-1}	b, atm	p (eO), atm	σ ohm^{-1} cm^{-1}
1000	7100	1.580	$6.13\cdot10^{-26}$	$1.02\cdot10^{-21}$
2000	4230	1.580	$9.58\cdot10^{-13}$	$9.50\cdot10^{-9}$
3000	3150	1.544	$2.74\cdot10^{-8}$	$1.99\cdot10^{-4}$
4000	2500	1.374	$3.41\cdot10^{-6}$	$2.02\cdot10^{-2}$
5000	2120	1.302	$4.31\cdot10^{-5}$	0.21
6000	1700	1.201	$2.15\cdot10^{-4}$	0.92
7000	1140	0.987	$6.65\cdot10^{-1}$	2.90
8000	800	0.835	$2.38\cdot10^{-3}$	8.33
9000	690	0.787	$8.32\cdot10^{-3}$	17.0
10000	620	0.755	$2.32\cdot10^{-2}$	28.0

This method was used to compute the current for three different forms of arc discharge in air. The results, together with the principal characteristics of the discharges, are given in Table 2. Although the discrepancies between the theoretical and observed currents are rather large, in all cases they scarcely exceed the errors of the experimental data themselves. Thus, in the first case the accuracy of measuring the plasma temperature and the concentration of Na in the air was such that the accuracy of the computations of the electron concentration N_e in which these measurements were used (and hence of the conductivity) was, according to the estimate of the author of [19, 20], 20-30%. In the second case the presence of an impurity did not affect the plasma conductivity, but the error in determining the temperature was ±200°K which gives an error in determining N_e (and σ) of the order of 25-30%. It should also be noted that the author of [21], making a supplementary measurement of the temperature at the axis of the arc by another method, obtained 6400°K instead of the value of 6150°K used in computing I. If this is the true temperature, then the computation of I from (4.1) gives a value very close to the true value of 10 a. In the third case, instead of measuring the impurity concentration, we measured the electron concentration directly with a precision of 5-10%. Accordingly, for the third case we also obtained the smallest discrepancy between the observed and calculated currents.

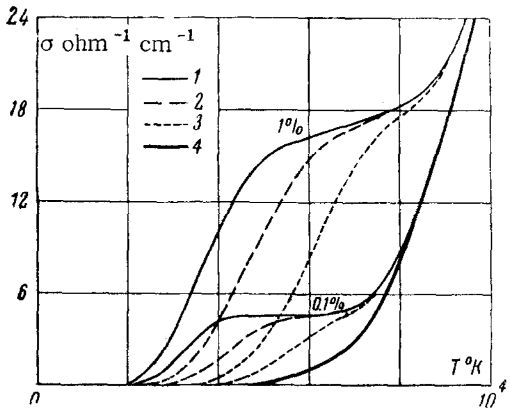

Fig. 3. Electrical conductivity of air with the following impurities: 1) cesium, 2) sodium, 3) magnesium, 4) air without impurities.

Table 2

Parameters of Arc Discharges in Air

№	Reference	Impurity	T_R, °K	T_0, °K	E, V/cm	I, a		$\frac{\Delta I}{I}$, %
						obs.	calc.	
1	[19, 20]	0.022% Na	2700	4750	19.5	4	5.2	+30
2	[21, 22]	0.01—1% C	4000	6150	17	10	6.3	—37
3	[23, 24]	30% C	7000	10900	10	200	213	+6.5

In conclusion, it should be noted that the method described is quite simple and, if the recommended data on the conductivity cross sections and the composition of air are used, entails an error of not more than 10-30%.

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20 June 1964 Irkutsk