MOBILITY OF IONS IN GAS MIXTURES

By R. E. Robson*

[Manuscript received 25 August 1972]

Abstract

A formula for the mobility of ions in a mixture of neutral gases is obtained as a generalization of an expression previously derived from the Boltzmann equation for ions in a pure gas (Kumar and Robson 1973). It is shown that Blanc's law holds only for very specialized situations. Using interaction potentials obtained in a previous work (Robson and Kumar 1973), the mobilities of K\(^+\) ions in helium–neon mixtures have been calculated and the deviations from Blanc's law are discussed.

I. INTRODUCTION

Recent experiments have shown that the mobility of potassium ions in neutral gas mixtures differs significantly from the predictions of Blanc's law (equation (1) below) and that the deviations are dependent upon the strength of the applied electric field, as well as upon the types and concentrations of the gases comprising the mixture (Milloy and Robson 1973). These deviations have been explained through a phenomenological theory, which is useful for providing an insight into the basic physical processes and which also gives good qualitative agreement with experiment (Milloy and Robson 1973, Sections 3 and 4). In the present paper we pursue a more rigorous approach and obtain an expression which enables computation of mobility in gas mixtures from a knowledge of the interaction potentials operating between the ion and each species of neutral molecule. This is done by generalizing a formula derived previously through solution of the Boltzmann equation for ions in a pure gas (Kumar and Robson 1973; hereinafter referred to as Paper I). Only the essential formulae are given and Paper I should be referred to for a more detailed discussion of the method and notation.

II. BOLTZMANN EQUATION FORMULA AND BLANC'S LAW

The ion mobility \( K \) is defined through the equation

\[
W = KE,
\]

where \( W \) is the drift velocity of the ions in the neutral gas and \( E \) is the applied electric field. Experimental data are normally given in terms of the reduced mobility \( \mathcal{K} \) which is defined by

\[
\mathcal{K} = \frac{n_0}{n_s}K,
\]

where \( n_0 \) is the density of the neutral gas and \( n_s = 2.69 \times 10^{19} \text{ cm}^{-3} \) is Loschmidt's

* Department of Theoretical Physics, Research School of Physical Sciences, Australian National University, Canberra; present address: Institute of Theoretical Physics, University of Alberta, Edmonton 7, Alberta, Canada.
Blanc's law may then be written as
\[ \mathcal{X}^{-1} = \sum_i x_i \mathcal{X}_i^{-1}, \]  
(1)
where \( x_i \) denotes the molar concentration of the \( i \)th neutral gas and \( \mathcal{X}_i \) is the reduced mobility in the pure gas \( i \) (see e.g. McDaniel 1964). It was shown in Paper I that solution of the Boltzmann equation by means of a polynomial expansion of the distribution function leads to the formula (Paper I, equations (I, 117) and (I, 118))
\[ \mathcal{X}_i = (e/n_e m)(M_i^{-1})_{01,01}, \]  
(2)
where \( e \) and \( m \) denote the charge and mass of the ion respectively and \( M_i \) is an infinite-dimensional matrix,
\[ M_i = (M_i)_{v_1 l_1, v_2 l_2} = (J_i)^{l_1}_{v_1 v_2} \delta_{l_1 l_2} + \mathcal{E} D_{v_1 l_1, v_2 l_2}. \]  
(3)
Here \( \mathcal{E} \) is a field parameter proportional to \( E/n_0 \) (equation (I, 111)), \( D \) is a matrix whose non-vanishing elements lie in blocks above and below the diagonal (equation (I, 97)), and the \( (J_i)^{l_1}_{v_1 v_2} \) denote the matrix elements of the Boltzmann collision operator for interactions between the ions and neutral molecules of type \( i \) (equation (I, 79)); \( v \) and \( l \) are Sonine and Legendre polynomial indices respectively which both run from 0 to \( \infty \) (\( v = 0 = l \) excluded). Some properties of the collision matrix \( J_i \) (see also Section IV of Paper I), which are important for a discussion of Blanc's law (1), are listed below.

(i) \( J_i \) is diagonal in the \( v \)-indices for a pure polarization (inverse fourth power) potential, that is,
\[ (J_i)^{l_1}_{v_1 v_2} = (J_i)^{l_1}_{v_1 v_1} \delta_{v_2 v_1}. \]  
(4)

(ii) For very heavy ions \( J_i \) is, to first order in the neutral-molecule–ion mass ratio, diagonal in \( v \) and thus equation (4) holds to a good approximation in this case also.

(iii) In general, for realistic potentials (e.g. the 12–6–4 potential of Mason and Schamp (1958) used in calculation below) and for arbitrary masses of ions and neutrals, off-diagonal elements of \( J_i \) are nonzero but are small compared with diagonal elements.

When the collision matrix is diagonal (and only then), the inverse matrix \( M_i^{-1} \) can be evaluated exactly at all fields, and in particular
\[ (M_i^{-1})_{01,01} = 1/(J_i)_{00} \]  
(equation (I, 155)). Thus, if (4) holds, equation (2) becomes
\[ \mathcal{X}_i = e/n_e m(J_i)^{1}_{00} \]  
(6)
and the mobility in the pure gas is independent of field strength. One would expect that it would also be true for gas mixtures if the ions interacted with all the neutral species through a polarization potential (or if the mass of an ion greatly exceeded the
molecular masses of all the neutral species), and, as we shall see, this is indeed the case.

In more realistic situations, the off-diagonal elements of $J_i$ introduce a field dependence which reflects the nature of the interaction potential; in such cases $M^{-1}$ can only be evaluated approximately by taking truncated matrices and, further, there are practical difficulties in treating high fields (Section IV of Paper I; Robson and Kumar 1973; hereinafter referred to as Paper II).

Equation (2) can be generalized to gas mixtures by replacing $J_i$ by

$$J = \sum_i x_i J_i.$$  

Thus

$$\mathcal{K} = \frac{(e/n_m)(M^{-1})_{01,01}}{0}$$  

(gives the reduced mobility of the ions in a mixture of neutral gases with concentrations $x_i$, and

$$M \equiv M_{v_1 l_1, v_2 l_2} = J_{v_1 v_2}^{l_1} + E D_{v_1 v_2}^{l_1}$$  

with

$$J_{v_1 v_2}^{l_1} = \sum_i x_i (J_i)^{l_1}_{v_2}.$$  

The matrix $J$ of equation (9) has properties similar to the $J_i$. For example, if all the $J_i$ are diagonal in $v$ then so is $J$, and analogously to equation (5) we have

$$(M^{-1})_{01,01} = 1/J_{00}^{l_1} = \left(\sum_i x_i (J_i)^{l_1}_{00}\right)^{-1}.$$  

(10)

Thus when equation (4) holds for all $i$, equation (7) becomes

$$\mathcal{K} = e\left(n_m \sum_i x_i (J_i)^{l_1}_{00}\right)^{-1}$$  

and mobility is again independent of field strength. It can be seen that equations (6) and (11) together give Blanc's law (1).

The approximate theory described by Milloy and Robson (1973) also predicts that Blanc's law holds when the mobilities in the pure gases are independent of field. That theory relates any deviations from Blanc’s law to variations of the mobilities in the pure gases with field. In the context of the present work, the field dependence results from nonzero off-diagonal elements of the collision matrix. Thus, for realistic potentials where the collision matrices are not diagonal, it can be anticipated that there will be departures from Blanc's law. In contrast to the qualitative theory of Milloy and Robson, we aim here at a quantitative analysis, i.e. we use equation (7) to calculate numerical values of mobilities directly from a knowledge of interaction potentials. These two approaches are complementary: the phenomenological theory provides a physical understanding of the problem while the formula (7) enables a more rigorous numerical investigation to be carried out.

At vanishing fields ($\mathcal{E} = 0$) it follows from equations (3) and (8), and the fact that off-diagonal elements of the collision matrices are small, that equations (5) and
(10) hold to a good approximation. Mobilities in the pure gas and in the mixture are then again (approximately) given by equations (6) and (11) respectively and Blanc's law should be quite accurate in this situation also. Again, this result is in accord with the phenomenological theory of Milloy and Robson (1973).

III. Deviations from Blanc's Law

The mobilities of K$^+$ ions in mixtures of helium and neon at room temperature (293 K) have been calculated using known K$^+$-helium and K$^+$-neon interaction potentials (Paper II, Section III). As could be expected, the mobility curves in mixtures lie intermediate between curves for pure helium and pure neon (Paper II, Figs. 4(a) and 4(b)). However, the main interest here is to determine the error associated with Blanc's law (1) as a function of $E/n_0$ and concentrations of the neutral gas components. This is shown in Figure 1. Although the deviations from Blanc's law can be seen to be quite small, they are nevertheless detectable with present day experimental techniques. As predicted in Section II above, Figure 1 shows that Blanc's law holds very nearly exactly at $E/n_0 = 0$. However, the deviations from the law increase with $E/n_0$ and show marked dependence upon the concentrations of the neutral gas components. Experimentally, it is observed that the deviations in the low and intermediate field regions are positive, as is the case in Figure 1; however, at higher fields ($E/n_0 \geq 40$ Td) the deviations become negative (Milloy and Robson 1973, Fig. 2). Unfortunately, because of the difficulties associated with computation of mobility from equation (1) at these high fields, only the lower extremity of experimental values of $E/n_0$ was covered in the present work. On the other hand, the phenomenological theory given by Milloy and Robson (1973) provides good qualitative agreement with experiment over a wide range of $E/n_0$ (Fig. 3 in their paper) but lacks the rigour of the present analysis.

IV. References