

The Application of Blanc's Law to the Determination of the Diffusion Coefficients for Thermal Electrons in Gases

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Abstract

Blanc's law is exactly applicable when the momentum transfer cross sections for electrons in each constituent of a gas mixture have the same energy dependence in the relevant energy range. This condition is rarely satisfied even for thermal energies. In this paper the magnitude of the errors arising from the applications of Blanc's law is examined for some cases where the condition is strongly violated, and a procedure developed for obtaining useful data from its application even under these circumstances.

1. Introduction

Accurate data for the diffusion coefficients for thermal electrons in gases provide a valuable check on the validity of the momentum transfer cross section at very low energies, typically from zero to 0.5 eV. For example, Gibson *et al.* (1973) used this method to check the validity of the e-He cross section derived from mobility measurements and used their result to reinforce the case for a further theoretical analysis of low energy scattering in helium. However, in several recent applications of the method used by these authors, namely the electron density sampling technique developed by Cavalleri (1969), it was not possible to make the measurements in a pure gas. In the work of Rhymes and Crompton (1975) (see also Rhymes 1976) a buffer gas was used to suppress the effect known as 'diffusion cooling' observed in experiments with pure argon, while in the work of Hegerberg and Crompton (1983) a buffer gas was used to suppress 'attachment cooling'. In such experiments the diffusion coefficient for the gas being investigated must be inferred from the diffusion coefficient measured in the mixture.

The motivation for the work described in the present paper was the need to analyse diffusion coefficient data from the experiments in mixtures of water vapour and nitrogen described in the following paper (Petrović 1986; present issue p. 249). For this work it was found to be necessary to employ a mixture technique in order to overcome a technical problem in measuring excessively large time constants with existing equipment.

The simplest way of deriving the 'unknown' diffusion coefficient from that measured in a mixture is to apply Blanc's law. However, in none of the cases cited above were the conditions satisfied that make the application of the law strictly valid.

Blanc's (1908) law was originally proposed to relate the mobilities of ions in gas mixtures to their mobilities in the separate components of the mixture. The law is strictly valid only for thermal ions (or electrons) and for gases in which the ratio of the momentum transfer cross sections in the constituents of the mixture is constant for all energies significantly represented in the thermal distribution.

While the law has found useful applications to ion mobilities, its application to electrons is more questionable on two counts. First, the momentum transfer cross section may be very different in both magnitude and energy dependence. Second, unlike ions, there are very few situations in which the electrons are nearly in thermal equilibrium with the gas. Nevertheless, Blanc's law has been applied to electron transport coefficients in mixtures (Verbeek and Drop 1974; Hegerberg and Crompton 1980, 1983; see also Long *et al.* 1976). In this paper we shall use the name Blanc's law specifically for the law as applied to diffusion coefficients for thermal electrons.

In the case of the measurements in $\text{H}_2\text{O}-\text{N}_2$ mixtures described in the companion paper (Petrović 1986), the cross sections were so different that it seemed likely that serious errors would result from the application of the law. An examination of the errors that can arise in this and other cases was therefore undertaken. Our primary aim was to examine its application to the determination of the density normalized diffusion coefficient for thermal electrons in a gas A (defined as ND^A) from data for the diffusion coefficient, ND^M , in a binary mixture containing gases A and B when the diffusion coefficient, ND^B , for component B is known. It would be difficult to find examples that meet the condition $\sigma_A/\sigma_B = \text{const.}$ which makes the law strictly applicable, but it has been argued (Hegerberg and Crompton 1980, p. 992) that 'for reasonably well behaved cross sections the deviation from Blanc's law is small even when this (identical energy dependence) condition is not fulfilled'. However, the question of the magnitude of the errors incurred in this application of the law when the condition is violated has not been studied. In Section 2 we make such a study and illustrate it in Sections 3 and 4 with calculations for some simple models and real gas mixtures. It is shown that Blanc's law, with its inherent simplicity, can be successfully used for this application even in unfavourable circumstances provided appropriate corrections are made.

2. An Analysis of the Application of Blanc's Law to Diffusion Coefficients for Thermal Electrons

(a) Basic Considerations

The formula for the density normalized diffusion coefficient for thermal electrons in a gas derived on the basis of the so called 'two term approximation' is (Huxley and Crompton 1974)

$$ND = \frac{2}{3}(2/\pi m)^{\frac{1}{2}}(kT)^{-\frac{3}{2}} \int_0^{\infty} \frac{\epsilon}{\sigma(\epsilon)} \exp(-\epsilon/kT) d\epsilon, \quad (1)$$

where $\sigma(\epsilon)$ is the momentum transfer cross section, m the mass of the electron, ϵ the electron energy, T the gas temperature and k Boltzmann's constant. For a binary mixture M with components A and B the effective cross section is

$$\sigma_M(\epsilon) = x\sigma_A(\epsilon) + (1-x)\sigma_B(\epsilon), \quad (2)$$

where x is the fractional abundance of A, and the diffusion coefficient for the mixture is therefore

$$ND^M = \frac{2}{3}(2/\pi m)^{\frac{1}{2}}(kT)^{-\frac{3}{2}} \int_0^\infty \frac{\epsilon \exp(-\epsilon/kT) d\epsilon}{x\sigma_A(\epsilon) + (1-x)\sigma_B(\epsilon)}. \quad (3)$$

If the ratio of the cross sections for the constituent gases is a constant such that $\sigma_A(\epsilon) = F\sigma_B(\epsilon)$, it follows that

$$ND^M = \frac{ND^B}{xF + (1-x)}, \quad (4)$$

and therefore that

$$\frac{1}{ND^M} = \frac{x}{ND^A} + \frac{1-x}{ND^B}, \quad (5)$$

which is Blanc's law for the diffusion coefficients. When ND^A is to be determined by an application of this law the more useful form is

$$ND^A = \frac{xND^M ND^B}{ND^B + (x-1)ND^M}. \quad (6)$$

In what follows the value of ND found from the application of Blanc's law in this way will be denoted by the appropriate subscript as ND_{BL} .

Equation (6) is derived on the assumption that the distribution function is the thermal Maxwellian ($E/N = 0$). If $E/N \neq 0$ then to the original condition that $\sigma_A(\epsilon)/\sigma_B(\epsilon) = \text{const.}$, we must add the additional one that the form of the electron energy distribution functions must be identical in the mixture and each of its constituents (see Milloy and Robson 1973).

(b) Deviations from Blanc's Law

The formulae for ND for the mixture and its components (equations 3 and 1) are such that it is not possible to derive a relationship similar to Blanc's law under circumstances other than the special case $\sigma_A(\epsilon)/\sigma_B(\epsilon) = \text{const.}$ On the other hand, the simplicity of the law (equation 5) is such that it is an advantage to retain it where possible even though this condition is not satisfied. Whether or not the application of the law is useful depends on the magnitude of the errors that result from its use. To examine this question we first consider the asymptotic behaviour of equations (3) and (6).

From equation (3) we get

$$\lim_{x \rightarrow 0} ND^M = ND^B \quad \text{and} \quad \lim_{x \rightarrow 1} ND^M = ND^A,$$

while from equation (6)

$$\lim_{x \rightarrow 1} ND_{BL}^A = ND^A,$$

$$\lim_{x \rightarrow 0} ND_{BL}^A = (ND^B)^2 / \left(\frac{2}{3}(2/\pi m)^{\frac{1}{2}}(kT)^{-\frac{3}{2}} \int_0^\infty \frac{\sigma_A(\epsilon)}{\sigma_B^2(\epsilon)} \epsilon \exp(-\epsilon/kT) d\epsilon \right). \quad (7)$$

Equation (7) was derived from equations (1), (3) and (6) using L'Hospital's rule.

The first three limits are obvious. The fourth is important for three reasons. First, it shows that ND_{BL}^A differs from ND^A unless $\sigma_A(\epsilon)/\sigma_B(\epsilon) = \text{const.}$ and therefore that, unless this condition is satisfied, this application of Blanc's law becomes less satisfactory as $x \rightarrow 0$. Second, equation (7) shows, perhaps surprisingly, that the divergence between the true value of ND^A and the value calculated from ND^M by an application of Blanc's law does not increase without limit as $x \rightarrow 0$. Finally, a comparison of the limiting value of ND_{BL}^A with ND^A calculated from equation (1) for specified energy dependences of σ_A and σ_B enables the maximum error resulting from the application of the law to be calculated.

(c) Errors Resulting from an Application of Blanc's Law and a Correction Procedure

In the previous subsection we showed that errors arise from an application of Blanc's law except under special (and unusual) circumstances. To investigate the magnitude of these errors when the law is used to determine ND^A from data for ND^M and ND^B , the procedure adopted was to first calculate the diffusion coefficients for gases A and B and for the mixture $xA + (1-x)B$ using the appropriate momentum transfer cross sections. Equation (6) was then used to calculate the Blanc's law prediction of ND^A (i.e. ND_{BL}^A) enabling the fractional error δ_{BL}^A to be calculated from

$$\delta_{BL}^A = (ND_{BL}^A - ND^A)/ND^A. \quad (8)$$

At this point we introduce the limiting error δ_{BL0}^A defined as the value of δ_{BL}^A as the abundance of gas A tends to zero, that is,

$$\delta_{BL0}^A = \lim_{x \rightarrow 0} \delta_{BL}^A. \quad (9)$$

Equation (7) was used to determine the limiting value of ND_{BL}^A in order to calculate δ_{BL0}^A . The importance of δ_{BL0}^A is that it can be calculated for any pair of gases and used as the indicator of when a simple application of Blanc's law leads to acceptably small errors in calculating ND^A from ND^M and ND^B , regardless of how small the fractional concentration of A may be.

With the aid of model calculations it will be shown in Section 3 that, even though δ_{BL0}^A is large, δ_{BL}^A may remain acceptably small provided x is not too small. In these circumstances it is possible to apply Blanc's law directly to obtain data of acceptable accuracy. On the other hand, when δ_{BL}^A is not small it follows from equation (8) that ND^A may be found from ND_{BL}^A by multiplying by a correction factor f , that is,

$$ND^A = f ND_{BL}^A, \quad (10)$$

where $f = 1/(1 + \delta_{BL}^A)$.

It should be noted that this procedure is applicable only under conditions where the uncertainty in the correction factor caused by uncertainty in the cross sections is small compared with the experimental uncertainty. Such conditions can be found for every mixture within a range of abundances, although this range may not be useful or accessible for some reason. However, because the cross sections need not be accurately known in order to calculate the correction factor reasonably accurately, the restriction to the range of mixture composition is often not serious. This is illustrated in Section 4.

3. Model Calculations

The results of calculations for two simple models are presented here in order to illustrate the limits of applicability of Blanc's law for determining ND^A to a required accuracy from mixture data. It should be stressed that, although these models are only illustrative, the first one approximates the situation for a mixture of two gases that have permanent dipole moments, that is, where the cross sections at low energies vary approximately inversely with the electron energy, while the second models a mixture of two gases for which the cross sections might loosely be described as having the same energy dependence.

(a) The first model comprises cross sections of the form

$$\sigma_A = A_0 \epsilon^{-a}; \quad \sigma_B = 20\epsilon^{-1}, \quad (11)$$

where σ is in 10^{-16} cm^2 when ϵ is given in eV.

The influence on the limiting error δ_{BLO}^A of different energy dependences for the cross sections may be shown by varying a . Since A_0 appears as a multiplicative factor in the expressions for $\lim ND_{\text{BL}}^A$ as $x \rightarrow 0$ (equation 7) and ND^A (equation 1), it follows from equations (9) and (8) that the limiting value of the error is not affected by the choice of A_0 . Thus we may put $A_0 = 20$ for this purpose. The results for a range of values of a are shown in Table 1. It can be seen that limiting errors larger than 1% occur only when the exponents in equations (11) differ by more than 20%.

Table 1. Errors in the values of ND^A derived by an application of Blanc's law to model (a)

a	1.5	1.2	1.1	1.05	1.0
	0.5	0.8	0.9	0.95	1.0
δ_{BLO}^A (%)	9.3	1.5	0.39	0.09	0

While the limiting error is independent of the value of A_0 , the approach to the limit as the abundance x of gas A decreases does depend on its value; the smaller the value of A_0 the more rapidly the maximum error is approached (Petrović 1982). This is because for a mixture of given composition the diffusion coefficient for the mixture contains progressively less information about component A as the collision frequency for that component decreases with respect to the collision frequency for the other, that is as $\langle \sigma^A(\epsilon) \rangle / \langle \sigma^B(\epsilon) \rangle$ decreases.

(b) For the second model the cross sections are

$$\delta_A = \sigma_{A0} + 20\epsilon; \quad \sigma_B = 20\epsilon. \quad (12)$$

The results for three values of σ_{A0} are presented in Fig. 1 which also illustrates the approach of δ_{BL}^A to an asymptotic limit as the fractional concentration of A decreases. When σ_{A0} is 0.01 the limiting error is only 0.4%, while for $\sigma_{A0} = 0.1$ it is 12%, and for $\sigma_{A0} = 1$ it is 47%. Here the important factor is the contribution of σ_{A0} to σ_A in the thermal energy range.

The model calculations illustrate two points. As previously stated, δ_{BLO}^A serves as an indicator as to whether or not Blanc's law can be applied to analyse data for any mixture of a pair of gases, but it would be useful to have a rule of thumb to

indicate when the law could be applied that did not depend on a calculation of $\delta_{\text{BL0}}^{\text{A}}$. This is desirable because of the labour involved in carrying out the integrations in equations (1) and (7) for each set of cross sections. Unfortunately, such a rule is not obvious. One might be tempted to assess the applicability without calculating $\delta_{\text{BL0}}^{\text{A}}$ by comparing approximate analytical expressions for the cross sections for the components, or by inspecting plotted or tabulated data, the law being considered to be applicable when the ratio of the cross sections appears to be approximately constant at all energies. However, the model calculations demonstrate the necessity of checking the applicability in every case. This is the first point. The second point, illustrated by the results for model (b) shown in Fig. 1, is that even though $\delta_{\text{BL0}}^{\text{A}}$ may be quite large, $\delta_{\text{BL}}^{\text{A}}$ may be acceptably small provided x is not too small.

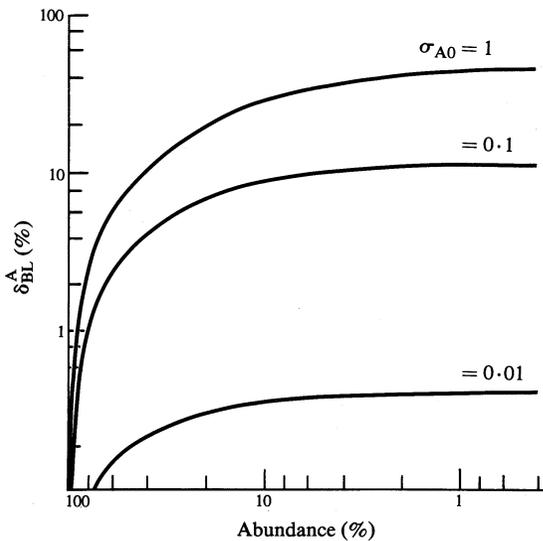


Fig. 1. Errors $\delta_{\text{BL}}^{\text{A}}$ made when Blanc's law is used to determine the diffusion coefficient for gas A from corresponding data for gas B and mixtures containing various fractional abundances x of gas A for model (b) (see equations 12).

4. Application to 'Real' Gases

In this section we discuss the application of Blanc's law to the analysis of diffusion coefficient data for several mixtures of real gases.

(a) Case 1

The first case considered provides an example of where it is justified to use Blanc's law to determine ND for one component of a mixture from measurements of ND for the mixture regardless of the mixture composition. This case, namely the case of mixtures of O_2 in N_2 , was chosen in the first instance in order to examine the validity of the procedure used by Hegerberg and Crompton (1983) to analyse their data for mixtures of these gases.

The cross sections of Lawton and Phelps (1978) for O_2 and of Pitchford and Phelps (1982) for N_2 were used to generate curves of $\delta_{BL}^{O_2}$ as a function of O_2 concentration. As can be seen from Fig. 2, for all concentrations of O_2 the calculated error is small enough (just larger than 1%) to justify the direct application of Blanc's law. Even in this case, however, one should be aware of the small systematic error that results from its application.

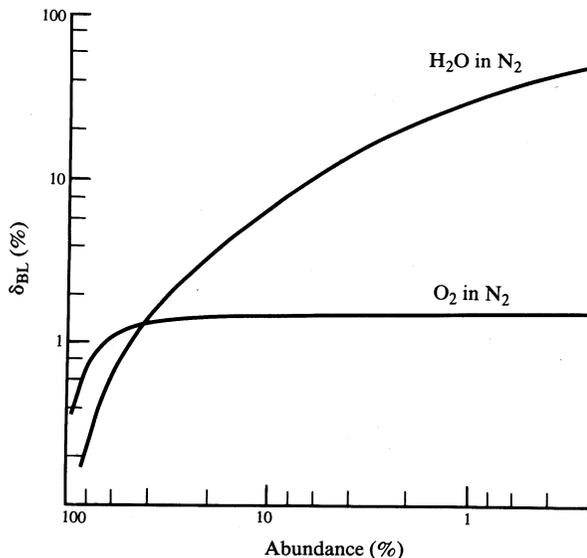


Fig. 2. Errors δ_{BL} made when Blanc's law is used to determine diffusion coefficients for H_2O and O_2 from the appropriate mixture data and the data for pure N_2 .

Hegerberg and Crompton's work provided a good example of a situation where the use of mixtures is essential for the application of a particular experimental technique. In this case its use avoided significant errors from attachment cooling in experiments based on the Cavalleri electron density sampling method. A similar situation occurs when one wants to suppress diffusion cooling in experiments based on the same technique (see Rhymes and Crompton 1975 and Rhymes 1976).

(b) Case 2

We consider next the case of the H_2O-N_2 mixtures used by Petrović (1986). As will be shown, this case provides an example of where Blanc's law cannot be validly applied for the purpose described above. For these calculations the cross section of Christophorou and Pittman (1970) for water vapour was used. This cross section was presented in the analytical form

$$\sigma_{H_2O}(\epsilon) = 23.84 \epsilon^{-1.085}. \quad (13)$$

It and the cross section of Pack *et al.* (1962) led to practically identical results for the error curves even though the experimental values of the thermal mobilities from which they were derived differ slightly (by about 2%). The results showing the variation of $\delta_{BL}^{H_2O}$ with H_2O concentration are shown in Fig. 2.

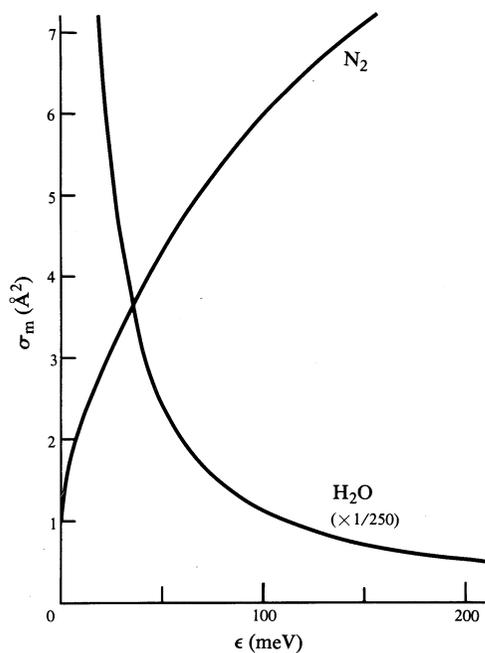


Fig. 3. Momentum transfer cross sections for electrons in N_2 and H_2O .

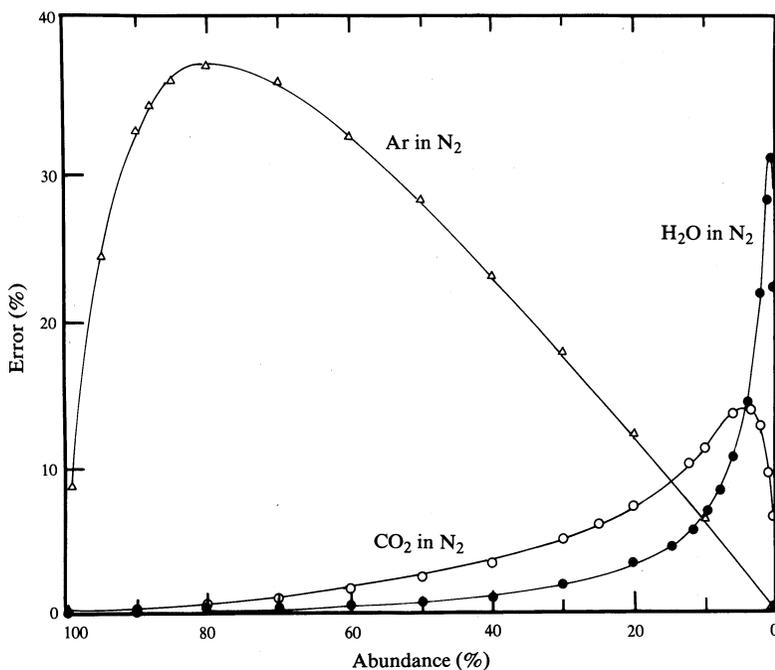


Fig. 4. Errors made when diffusion coefficients for thermal electrons in H_2O-N_2 , CO_2-N_2 and $Ar-N_2$ mixtures are calculated using Blanc's law and the data for the pure gases. Sources of data for the cross sections additional to those quoted in the text are Kieffer (1973) for CO_2 and Haddad and O'Malley (1982) for Ar.

An important point in applying the correction procedure described in Section 2c is the sensitivity of the correction factors to the cross sections used to calculate them. We can use the calculations for the H₂O–N₂ mixtures as an example, assuming that the N₂ cross section is known but that there is uncertainty in the normalization factor for the H₂O cross section. Accordingly the multiplicative constant in equation (13) was changed by 10%. In the case of the 10% H₂O–90% N₂ mixture the 7% correction (see Fig. 2) was changed by less than 0.25%. Thus, when the uncertainty in the cross section is of this order, negligible error in the derived value of *ND* results from the application of Blanc's law to the mixture data, provided the calculated correction is applied. This example illustrates the point that, even in the case when the cross sections differ by as much as those for N₂ and H₂O (see Fig. 3), an appropriate choice of the mixture composition enables the mixture data to be analysed in this way without the necessity of a high order of accuracy in the cross sections. For example, if the mixture composition were such that the correction is approximately 30%, the cross-section data would need to be known to better than 10% for the accuracy of the correction to match the experimental accuracy, but if the correction factor were of the order of 5% the cross sections could be uncertain by up to 50%, yet still be sufficiently accurate for this purpose.

(c) Case 3

Finally, it is important to illustrate the errors that can arise when Blanc's law is used to calculate the diffusion coefficient for a mixture from the diffusion coefficients for its constituents. Some typical examples are shown in Fig. 4. Here the diffusion coefficients for the constituents were first calculated from published cross sections and these data used together with Blanc's law to calculate the diffusion coefficient for mixtures of varying composition. Equation (3) was then used to calculate the 'true' diffusion coefficients for the same mixtures, and the differences, expressed as percentages of the 'true' values, plotted as functions of the compositions of the mixtures. As can be seen, the application of the law can lead to large errors in those cases where the energy dependences of the cross section are very different, for example in mixtures of argon and nitrogen.

5. Conclusions

In this paper we first discussed the application of Blanc's law to the determination of diffusion coefficients for thermal electrons in a gas from experimental data for a mixture containing that gas. A number of calculations for both model and real gases show that considerable errors may result from an application of the law, especially for low abundances of the gas. These errors are caused by different energy dependences of the momentum transfer cross sections for the constituents. However, it has been shown that it is possible to apply the law with appropriate correction factors even when the cross sections are as dissimilar as those for H₂O and N₂. It has also been shown that such a procedure is remarkably accurate even though the available cross-section data may not be highly accurate. Thus, for a gas for which the momentum transfer cross section in the thermal region has not been well established, the use of this procedure enables a value of the density normalized diffusion coefficient to be determined that is much more accurate than the value that could be calculated from the cross section. In addition, it has been shown that significant, and sometimes large, errors are made when the law is used to calculate the diffusion coefficient for a mixture from the corresponding data for its constituents.

Two further points may be noted, both concerning the relation of this to other recently published work. First, our conclusions based on model calculations are somewhat different from those reached by Milloy and Robson (1973) and Whealton *et al.* (1974). However, the momentum transfer theory used by these authors breaks down at thermal energies since the momentum and energy balance equations upon which it is based are not strictly applicable when the influence of the electric field no longer dominates.

Second, the examples discussed at the end of Section 3 are relevant to the recent paper by Chen and Jones (1984). These authors discussed the application of Blanc's law to mobilities in gas discharges, in particular the case of discharges in argon-mercury mixtures. Relatively simple formulae for the temperature dependences of electron mobilities were then derived on the basis of simplified formulae for the momentum transfer cross sections. Subsequently, instead of using Blanc's law they derived a formula for the conductivity of an arbitrary mixture, which is the sum of the conductivity of argon and a correction factor which includes the overall influence of the presence of mercury. Since their procedure necessarily depends on numerical integration, it would seem preferable to use Blanc's law and apply a correction. This procedure would also enable one to use experimental mobilities for pure gases, and thus obtain a very accurate result for the mixture even though the cross sections used to calculate the corrections were not as accurate as the mobilities. In contrast, the procedure suggested by Chen and Jones is restricted by the accuracy of the assumed analytical forms of the cross section which, for example, were unable to include the resonance in the vicinity of 2 eV (Elford 1980).

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