

THE DRIFT VELOCITY OF POTASSIUM IONS IN HYDROGEN AT 293°K*

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Although there exists a large body of data for the drift velocity of positive ions in gases (Loeb 1955; McDaniel 1964), some of the data are conflicting or ambiguous due to uncertainty concerning the identity of the ion being studied (Dalgarno, McDowell, and Williams 1958; Davies *et al.* 1966). This ambiguity is particularly serious in the case of atomic or molecular ions moving in the parent gas, since ion-molecule reactions may occur in the ion source or within the drift chamber. The necessity for simultaneous drift velocity measurements and ion identification has led a number of workers (e.g. Edelson and McAfee 1964; Keller, Martin, and McDaniel 1965; Madson, Oskam, and Chanin 1965; Saporoschenko 1965) to design experiments in which such identification is possible. In these experiments the gas pressure in the drift chamber is of the order of a few torr while that in the mass spectrometer is usually less than 10^{-5} torr.

There are two ways in which the pressure differential has been achieved. The first is to use a very small exit hole (of the order of 4×10^{-3} cm in diameter) in the electrode that separates the drift chamber from the mass spectrometer (e.g. Edelson and McAfee 1964; Saporoschenko 1965), while the second is to use a much larger exit hole and differential pumping (e.g. Keller, Martin, and McDaniel 1965). The second method is used when ions with energies close to thermal energy are being studied, since high energy collisions within the transition region, as can occur using the first method, may change the identity of the ion. Because of the large attenuation of the ion current in the transition from the drift chamber to the mass spectrometer, the diameter of the exit hole of the drift chamber has usually been chosen to be not less than about 0.08 cm. Even with moderately large pumping systems, this requirement restricts the pressures that can be used in the drift chamber to less than about 2 torr, and measurements are often made at pressures less than 0.5 torr. Pressures in this range are difficult to measure with high accuracy. In addition there are problems such as pressure stability and thermal gradients that must also be considered.

In systems in which no identification is made, i.e. static systems, much higher gas pressures can be used thus enabling accurate pressure measurements to be made. In addition, pressure stability and thermal gradients present no problems. In view of the much greater complexity and the additional sources of error that are incurred in measurements of drift velocities of mass identified ions, it is desirable to be able to check the accuracy of these more complex systems against a set of data of high accuracy obtained in a static system. To provide such data, measurements

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have been made of the drift velocity of potassium ions in hydrogen at 293°K. Since these measurements were made in a drift tube with no provision for direct mass identification, the identity of the ion requires special consideration (see later).

Apparatus

The potassium ion source used was of the type described by Blewett and Jones (1936). This source is easily manufactured and emits singly charged ions of one species. A difficulty sometimes encountered when using these thermionic sources is the presence of ions emitted from the tungsten wire spiral that acts as the heater. This does not present a problem in the present case since, at low operating temperatures, the spurious emission consists almost entirely of potassium ions.

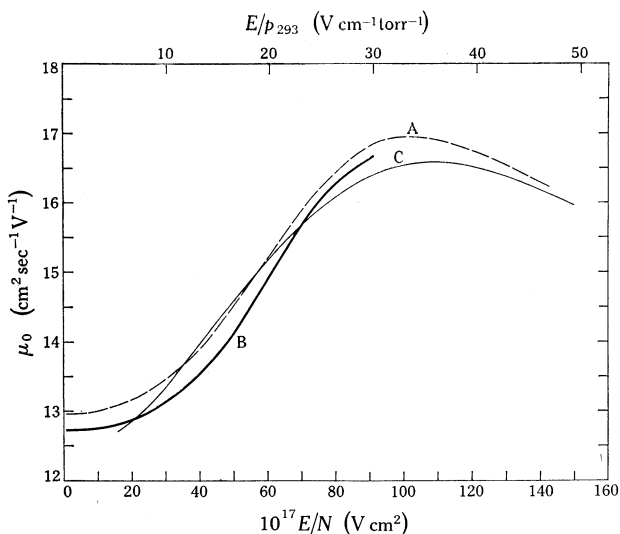


Fig. 1.—The mobility μ_0 of potassium ions in hydrogen. Curve A, Albritton (301°K); curve B, presents results (293°K); curve C, Hershey.

The gas used was hydrogen since it can be readily obtained with an impurity level of less than 0.1 p.p.m. (Young 1963) by diffusion through palladium.

The apparatus and experimental technique were identical to those described previously (Elford 1966; Crompton, Elford, and Jory 1967). The gas pressures used were 1, 2, 10, 20, and 50 torr and the range of values of E/N was from 0.61×10^{-17} to 9.1×10^{-16} V cm². The experimental tube was maintained at 293°K throughout the measurements.

Results and Discussion

The experimental results are shown in Table 1 and Figure 1. The reduced mobility μ_0 is defined by

$$\mu_0 = \frac{W}{760(E/p_0)} \quad \text{cm}^2 \text{sec}^{-1} \text{V}^{-1},$$

where W is the ion drift velocity (cm/sec), E is the electric field strength (V/cm), and p_0 is the reduced pressure defined as

$$p_0 = p_T(273/T) \quad \text{torr.}$$

In Figure 1 the present experimental points all lie within the thickness of the curve and have therefore not been shown.

The mobility extrapolated to zero electric field strength is $12.75 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ and was obtained by averaging the best estimate of the mobility at the 10 lowest values of E/p_{293} shown in Table 1. The error in the zero field mobility is considered to be less than 0.3%.

These measurements are subject to two sources of systematic error. Errors may arise from contact potential differences between the two electrical shutters and from diffusion errors of the type described by Lowke (1962). To reduce the effect of contact potential differences, no measurements were made with electric field strengths less than 3 V/cm, and when the "best estimate" values were obtained they were weighted in favour of those taken at the higher electric field strengths.

The diffusion error can be calculated from the equation

$$W' = W \left(1 + \frac{C}{d(W/D)} \right),$$

where W is the true drift velocity, W' is the measured drift velocity, d is the drift distance, D is the diffusion coefficient, and C is a constant. The value of C has been discussed by Crompton, Elford, and Jory (1967) and for the present apparatus has been shown to be 1.5. The diffusion error is less than 0.1% at all the pressures used. Since at any value of E/N the diffusion error decreases with increasing gas pressure, the best estimate results were weighted in favour of the results taken at the higher gas pressures.

The drift velocity data are considered to be in error by less than 0.3% for $E/p_{293} < 20 \text{ V cm}^{-1} \text{ torr}^{-1}$ and less than 0.5% for $20 < E/p_{293} < 30 \text{ V cm}^{-1} \text{ torr}^{-1}$.

Two other sets of measurements of the drift velocity of potassium ions in hydrogen are available. The most recent, those of Albritton (1967), were taken with mass identified ions, using the experimental method of Keller, Martin, and McDaniel (1965), but with an experimental tube of improved design and performance (Albritton *et al.* 1967).

The only other data available are those of Hershey (1939), who used the Townsend magnetic deflection method. No provision was made to identify the ion present. Hershey measured the ion mobility at three gas pressures, 2.7, 0.85, and 0.25 torr, but found that the mobility varied with gas pressure at constant values of E/N . He considered that this variation was due to an inadequacy in his theoretical analysis of the motion of the ions and that as a consequence his low pressure mobility measurements were meaningless. Hershey suggests that the true mobility is probably slightly higher than the values obtained at the highest gas pressure for values of E/p_{293} greater than about $20 \text{ V cm}^{-1} \text{ torr}^{-1}$. For this reason only the curve given

by Hershey for the highest pressure (2.7 torr) has been shown in Figure 1. It should be noted that Hershey's data have been corrected to correspond to standard gas density (760 torr, 273°K).

No data for the variation of the mobility of potassium ions with E/N are available from the measurements of the Bristol group (Tyndall 1938), but the zero field mobility for potassium ions in hydrogen is listed by Tyndall as $13.5 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$. This value when converted to standard gas density is $12.6(6) \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ and is in good agreement with the present value of $12.75 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$.

Ion Identification

Since no direct identification of the ion was possible in the present work it is necessary to establish from other evidence that the ions whose drift velocity was measured were singly charged potassium ions. The following facts support the present identification of the ions. Firstly, the emission from sources made from the same materials and by the same technique was examined with a quadrupole mass spectrometer. The emission consisted of K^+ ions, the only other ions detectable being Na^+ to the extent of approximately 1%. Secondly, although the resolving power of the apparatus used to measure the drift velocity was insufficient to detect the presence of any other alkali ions, it would have been sufficient to detect clustered ions if they had been present (e.g. Tyndall 1938, p. 52). No ion of lower mobility (i.e. a clustered ion) was found during the measurements. Thirdly, there is good agreement (of the order of 2%) between the results of Albritton (1967), in which the ions were directly identified as K^+ , and the present measurements.

On the basis of the evidence there would seem to be little doubt concerning the identity of the ion observed in the present measurements. However, the necessity for the discussion above reinforces the importance of directly identifying the ion when drift velocity measurements are made.

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