THE EFFECT OF CLUSTERING ON THE MEASUREMENT OF THE MOBILITY OF POTASSIUM IONS IN NITROGEN GAS*

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McDaniel and Martin (1971) have suggested that the zero-field reduced mobility of (unclustered) K^+ ions in nitrogen at room temperature and low pressures ($\sim 0 \cdot 1$ torr) is accurately enough known to be useful in pressure calibration of drift tubes and other types of apparatus employed in atomic collision experiments, where the uncertainty in the value of the gas pressure frequently represents the largest source of error in the measurements. Elford (1971) has questioned the validity of this suggestion on the grounds that he has observed a very slight, explicit dependence of the reduced mobility of K^+ ions on the gas pressure in drift tube experiments with nitrogen and other gases. Although this pressure effect cannot be reconciled with existing mobility theory (McDaniel and Mason 1972), Elford believes the effect to be real and hence maintains that in fact the true mobility of unclustered K^+ ions in nitrogen is not accurately known. The purpose of this communication is to point out that Elford's experiments with nitrogen were conducted at pressures sufficiently high that significant clustering of nitrogen molecules with his K^+ ions inevitably occurred and that consequently the suggestion of McDaniel and Martin (1971) is not weakened by his findings.

Elford (1971) discussed the possibility that the pressure effect in his measurements on nitrogen was attributable to his K^+ ions spending a fraction of their drift time clustered with nitrogen molecules, according to the reversible reaction

$$K^+ + N_2 + N_2 \rightleftharpoons (K^+N_2) + N_2 \,.$$

It is reasonable to assume that the mobility of the cluster (K^+N_2) is lower than that of the bare ion K^+. If this assumption is correct and if clustering were occurring in Elford's experiments, then we would expect the observed reduced mobility of the charge carriers to decrease as the pressure, and hence the fraction of the time the ions spent in clustered form, was increased. Elford did indeed observe that the reduced mobility decreased with increasing gas pressure. However, he dismissed the clustering explanation, partly on the grounds that only one set of ion current maxima was observed in his plots of current versus shutter frequency. Elford further cited the fact that he could not detect any clustered ions when, in auxiliary experiments, he attached a mass spectrometer at the end of the ionic drift path to sample the emerging ions. (The range of gas pressure covered in these auxiliary experiments was not

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indicated.) Elford (1971) also accurately stated that Moseley *et al.* (1969) had failed to observe clustered ions in experiments with K^+ ions in nitrogen performed in our laboratory.

The fact that we did not detect clusters in our drift tube mass spectrometer experiments reported in 1969 cannot be adduced as evidence supporting Elford's argument. Our measurements were made at very low pressures (0·052–0·836 torr) where the concentration of clustered ions is extremely small, although it is now known to be finite. Indeed, in recent studies of K^+ ions in nitrogen at low E/N and 300 K, we have observed (K^+N_2) clusters at pressures as low as 0·1 torr (1 ion in 2×10^3 was clustered at this pressure). Elford's failure to observe clustered ions is difficult to explain because his measurements were made at much higher pressures (1·44–18·8 torr), and the relative abundance of the clusters increases linearly with the gas pressure. Beyer and Keller (1971) have studied K^+ ions in nitrogen at 310 K with a drift tube mass spectrometer, and they observed clustering down to their lowest pressure (0·5 torr).* Their equilibrium constant for the clustering reaction (which was based on measurements at pressures up to 2·0 torr*) implies that at low E/N about 10% of the K^+ ions in nitrogen should be clustered at a given instant at Elford's highest pressure, or alternatively stated, that each K^+ ion should spend about 10% of its drift time in clustered form at that pressure.

In view of the evidence presented here, it would appear that Elford's ions spent a fraction of their drift time in clustered form throughout his entire pressure range, and that his observed reduced mobility should have been expected to decrease with increasing pressure due to clustering. Hence Elford's conclusion that the reduced mobility of *unclustered* K^+ ions depends explicitly on the nitrogen gas pressure would appear to be based on insufficient evidence.

Since Elford's (1971) measurements did not relate to ions which remained unclustered throughout their drift, the suggestion of McDaniel and Martin (1971) would still seem to be reasonable for calibrations conducted at the suggested low pressures, where clustering is not appreciable and where the zero-field mobility of K^+ ions in nitrogen does appear to be known to within 0·5%. Of course it is not suggested that the method proposed by McDaniel and Martin be used if greater accuracy of pressure calibration is desired, or that it be used at pressures high enough for clustering to be a factor. It is interesting to note that, when Elford's mobilities at a given E/N are extrapolated to 0·1 torr pressure and the resulting values for the various E/N are averaged, a mobility is obtained which is less than 0·6% below the value of $2\cdot54\ cm^2\,V^{-1}\,s^{-1}$ suggested by McDaniel and Martin for use in pressure calibration.

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* Keller (personal communication).

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