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The Mobility of K^+ Ions in Helium and Argon

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Abstract

A drift tube–mass spectrometer has been used to measure the mobility of K^+ ions in helium at 294 and 80 K over the E/N range 5–60 Td and in argon at 295 K over the E/N range 3–120 Td. The zero field reduced mobility κ_0 for K^+ in He was determined to be $21 \cdot 14 \pm 0 \cdot 11\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ at 294 K and $17 \cdot 32 \pm 0 \cdot 26\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ at 80 K. The value of κ_0 obtained for K^+ in Ar at 295 K is $2 \cdot 640 \pm 0 \cdot 013\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$. The results are compared with those obtained in previous measurements.

1. Introduction

The derivation and testing of interaction potentials for ion–atom systems by the analysis of mobility data is a well established procedure (see e.g. Viehland 1984) and relies on the availability of mobility data of high precision. Ideally the data should cover a wide range of E/N values (where E is the electric field strength and N the gas number density) and be taken at sufficiently low gas temperatures T that the mobility is determined only by the dipole polarization force between the ion and atom. The aim of the present work was to measure the mobility of K^+ ions in helium at both 294 and 80 K to provide not only data of higher precision for analysis but also data which are more sensitive to the long range part of the potential than that available previously. In the case of K^+ ions in argon at 295 K the purpose was to improve on the accuracy of the data presently available in order to reduce the uncertainty in potential derivations.

The present work is an extension of that carried out by Cassidy and Elford (1985) for the case of Li^+ ions in helium and argon.

2. Apparatus

The drift tube–mass spectrometer, which employed the Bradbury–Nielsen time-of-flight technique, and the measurement procedure have been described by Cassidy and Elford (1985) and will not be further discussed here. Only those features relevant to the use of K^+ ions in this work will be considered.

The K^+ ions were obtained by thermionic emission from a bead of potassium alumino silicate mounted on a tungsten spiral heater (Blewett and Jones 1936).

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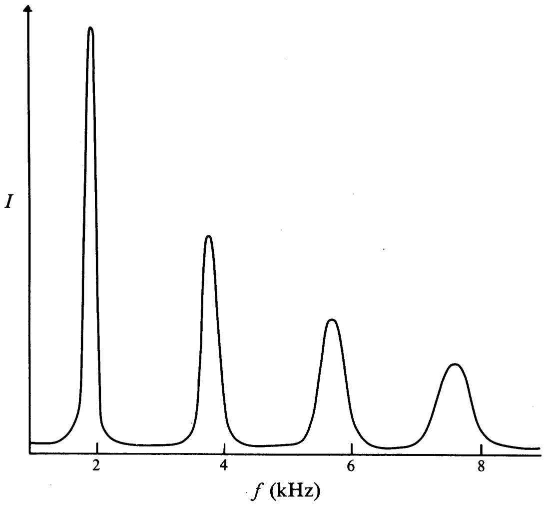
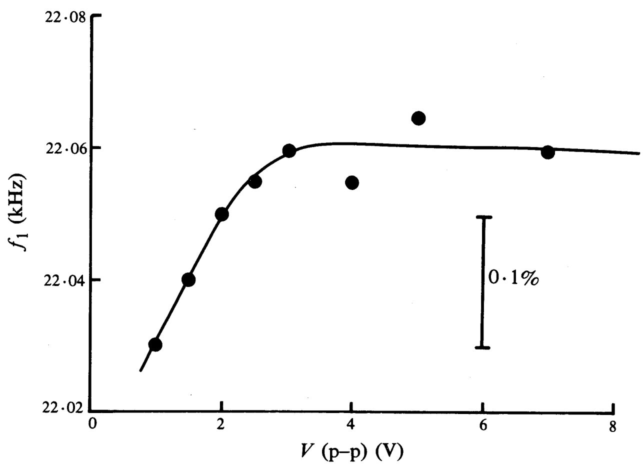


Fig. 1. Typical variation of collector current I with frequency f of the sinusoidal shutter signal (i.e. an arrival time spectrum) for K^+ ions in helium. Conditions were 6 Td, 0·413 kPa, 294 K and drift distance 9·008 cm. All data points lie within the thickness of the curve.

Fig. 2. Variation of the frequency f_1 at which the ion current is a maximum as a function of the amplitude of the sine wave signal applied to the shutter grids.



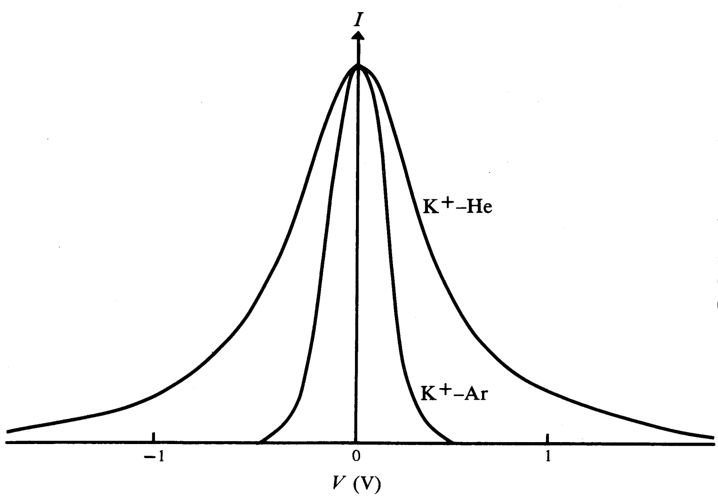


Fig. 3. Variation of the ion current transmitted by a shutter as a function of the potential difference between adjacent grid wires (i.e. cutoff curve), at 6 Td and 0·134 kPa, for K^+–He and K^+–Ar.

A typical arrival time spectrum is shown in Fig. 1 for K^+ ions in helium at an E/N value of 6 Td (1 Td $\equiv 10^{-21}$ V m^2). No product ions were observed in the arrival time spectrum or by using the mass spectrometer. The measured ion drift velocities were independent of the value of E/N in the region before the first shutter and of the amplitude of the sinusoidal gating signal applied to the Bradbury–Nielsen grids (Fig. 2). Most of the drift velocity data for K^+–He (294 K) and K^+–Ar (295 K) were taken with the 9·008 cm drift distance but a number of measurements were made with the 3·001 cm drift length to test for any dependence on drift length. No dependence was found to within the experimental scatter ($<\pm 0{\cdot}2\%$). In the case of K^+–He (80 K), the development of thermal gradients due to the operation of the filament made measurements with the 9 cm drift distance inaccurate and all the data were taken with the 3 cm drift distance. Checks made early in a series of measurements (before the heat produced by the filament led to a large temperature gradient in the drift region) showed that the drift velocities measured with the two drift distances generally agreed to within 0·5%, any difference being attributed to a temperature difference. Data taken manually or by using the data acquisition system agreed to within the experimental scatter.

In the case of Li^+–He, Cassidy and Elford (1985) found that the range of pressures and E/N values that could be used was determined by the failure of the Bradbury–Nielsen shutters to operate satisfactorily. This limitation was not found in the present work with K^+ ions, although the shutter operation was more efficient in argon than in helium. The shutter operation is characterized by the 'cutoff curve', i.e. the variation in transmitted current with the potential difference between adjacent wires of the shutter grid. Fig. 3 demonstrates the better efficiency of the grids in the case of K^+ ions in argon compared with that of K^+ ions in helium, for the same pressure and E/N values.

The lowest value of E/N at which measurements could be made was limited by the signal-to-noise ratio in the measured current, the collected ion current decreasing rapidly as the value of E/N in the drift region was reduced. The upper limit to the value of E/N at a given gas pressure was generally set by the onset of discharge in the drift region.

3. Results

The reduced mobility κ was obtained from the measured drift velocity v_{dr} by using the relation

$$\kappa = \frac{v_{dr}}{E/N}\,\frac{1}{N_s},$$

where $N_s = 2{\cdot}6868\times10^{19}$ cm^{-3}. All values of κ given in the present paper are in units of cm^2 s^{-1} V^{-1} and all values of E/N are in Td. In Section 4, where the present data are compared with those obtained previously, none of the present data points are shown as they all fall within the thickness of the curves.

(a) Results for K^+–He

The reduced mobility of K^+ ions in helium at 294 K was obtained at E/N values from 5 to 60 Td and at pressures in the range 0·134–0·413 kPa (Table 1 and Fig. 4*a*). At very low values of E/N and the lowest pressure there is evidence of upcurving in the data, indicating the presence of a minor shutter contamination problem

Table 1. Reduced mobility of K^+ ions in helium at 294 and 80 K

Data at 294 and 80 K were taken with 9 and 3 cm drift distances respectively

E/N (Td)	κ at p (kPa) of 0·0725	0·134	0·279	0·413	Best estimate	E/N (Td)	κ at p (kPa) of 0·0725	0·134	Best estimate
		At 294 K				12·0	18·08	18·04	18·06
						12·63	18·16		
5·0		21·23	21·15	21·13	21·14	13·0		18·21	18·21
8·0		21·21	21·16	21·15	21·15	13·26	18·29		18·29
10·0		21·19	21·20	21·17	21·19	14·0		18·37	18·37
12·0		21·22	21·20	21·20	21·21	14·13	18·43		18·43
15·0		21·22	21·22	21·22	21·22	15·0	18·64	18·61	18·61
20·0		21·17	21·20		21·20	16·0		18·81	18·81
25·0		21·01	21·04		21·04	17·0	19·10	19·04	19·07
30·0		20·74			20·74	17·5		19·15	19·15
40·0		19·96			19·96	20·0	19·81		19·81
50·0		19·09			19·09	22·0	20·29		20·29
60·0		18·24			18·24	24·0	20·63		20·63
						25·13	20·69		20·69
		At 80 K				26·11	20·87		20·87
2·0		17·20	17·30	17·32	17·31	27·11	20·93		20·93
3·0		17·27	17·33	17·35	17·32	28·12	21·00		21·00
4·0		17·31	17·34	17·36	17·33	29·12	21·01		21·01
5·0		17·35	17·37		17·36	30·16	20·98		20·98
6·0		17·43	17·43		17·43	31·0	21·01		21·01
7·0		17·47	17·48		17·48	32·20	20·96		20·96
8·0	17·54	17·54	17·53		17·54	33·21	20·92		20·92
9·0		17·64			17·64	34·21	20·84		20·84
10·0	17·80	17·69				35·2	20·78		20·78
11·0		17·89			17·89				

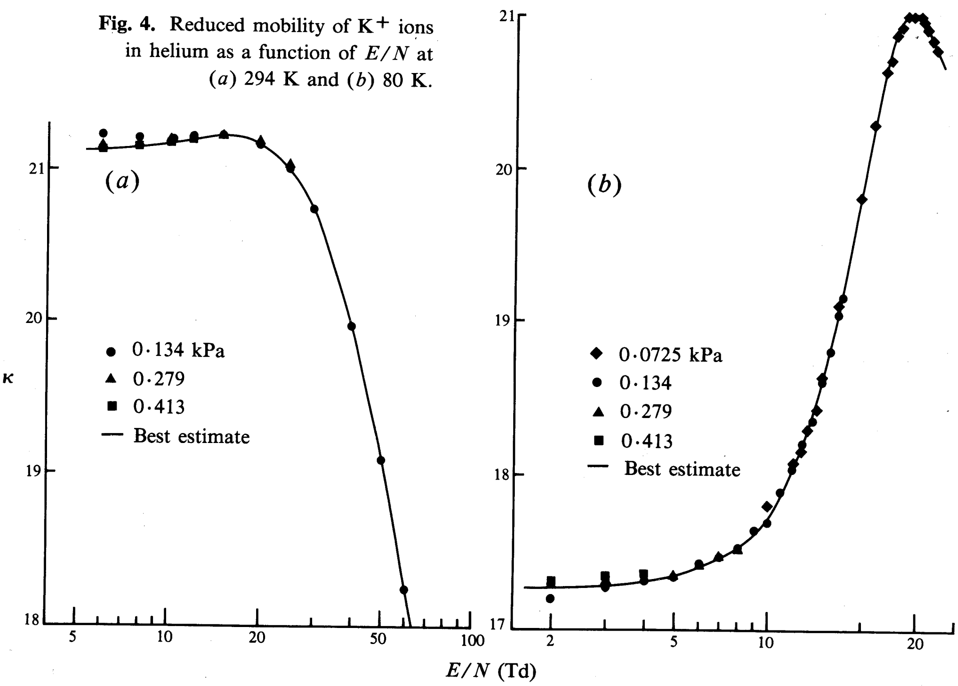


Fig. 4. Reduced mobility of K^+ ions in helium as a function of E/N at (*a*) 294 K and (*b*) 80 K.

Table 2. Reduced mobility of K^+ ions in argon at 295 K

Values in parentheses were taken with the 3 cm drift distance; all other values were taken with the 9 cm drift distance

E/N (Td)	κ at p (kPa) of 0·0724	0·134	0·279	0·413	Best estimate
3·0				2·640	
5·0			2·642	2·637 (2·646)	2·647
6·0		2·649			
7·0		2·648		2·643 (2·642)	
8·0		2·647	2·639 (2·645)	2·638 (2·641)	2·647
10·0	2·659	2·649	2·643 (2·644)	2·641 (2·642)	2·647
12·0	2·663	2·653	2·647 (2·648)	2·643 (2·641)	2·653
15·0	2·668	2·655 (2·657)	2·650 (2·651)	2·647 (2·643)	2·655
20·0	2·676	2·668	2·664 (2·659)		2·668
25·0	2·687	2·684	2·677 (2·674)		2·684
30·0	2·706	2·703			2·703
35·0	2·736	2·729			2·729
40·0	2·771	2·762			2·762
45·0	2·808	2·800			2·800
50·0	2·846	2·838			2·838
60·0	2·935	2·930			2·930
70·0	3·020				3·020
80·0	3·093				3·093
90·0	3·153				3·153
100·0	3·193				3·193
110·0	3·210				3·210
120·0	3·217				3·217

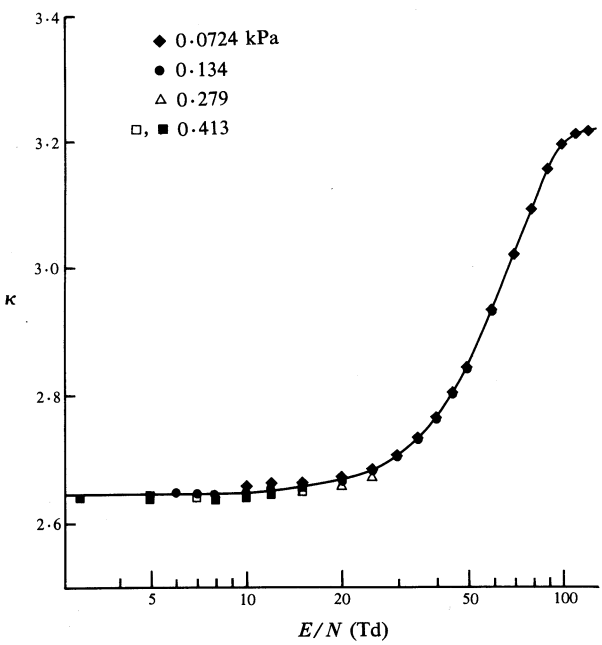


Fig. 5. Reduced mobility of K^+ ions in argon as a function of E/N at 295 K. Full and open symbols are values taken with drift distances of 9 and 3 cm respectively.

(Elford and Milloy 1974). Under these conditions the arrival time spectra were skewed and poorly resolved. The remaining data show no dependence on the drift distance or pressure. The data for K^+ ions in helium at 80 K were obtained at pressures between 0·0725 and 0·413 kPa and at E/N values between 2 and 35 Td (Table 1 and Fig. 4*b*).

(b) Results for K^+–Ar

The reduced mobility of K^+ ions in argon at 295 K was measured at pressures from 0·0724 to 0·413 kPa and E/N values from 3 to 120 Td (Table 2 and Fig. 5). Data were taken with both the 3 and 9 cm drift distances, although wider ranges of pressures and E/N values were attainable with increased resolution of the arrival time spectrum by using the 9 cm drift distance. The data show slight evidence for upcurving at low values of E/N (below 8 Td at 0·134 kPa and below 3 Td at 0·413 kPa) but the effect is small and within the experimental scatter.

The results for the reduced mobility of K^+ ions in argon at 295 K show a small pressure dependence, of the type observed by Elford and Milloy (1974), attributed to temporary ion complex formation

$$K^+ + Ar \rightleftarrows (K^+ . Ar)^* .$$

The change in mobility for a change in pressure from 0·134 to 0·413 kPa was 0·3%. The results were unchanged after a regild of the shutters, indicating that the pressure dependence was not due to the presence of shutter contamination.

(c) Errors

The main source of error in the reduced mobility arises from the determination of the gas temperature. This error is estimated to be 1·0% at 80 K but reduces to 0·1% at room temperature. Other sources of error are the determination of the potential difference between the shutters (random 0·02%, systematic error 0·06%), the determination of the gas pressure (random 0·02% increasing to 0·04% at 0·0724 kPa; systematic 0·1%), and the determination of the effective transit time of the ions between the shutters. This is estimated to be 0·1% at room temperature and 0·2% at 80 K. The estimates given here are for maximum errors. The total errors for the reduced mobility of K^+ ions in helium and argon are estimated to be 0·5% at 294 K and 1·5% at 80 K. The error limits were calculated by adding the systematic errors arithmetically and the random errors in quadrature. The total error is taken to be the sum of the total random and systematic errors.

4. Comparisons with Previous Mobility Measurements

(a) Comparison of K^+–He Results

The present best estimate values of the reduced mobility for K^+ ions in helium at 294 K are compared with those of previous workers in Fig. 6. The present results show a previously unobserved maximum in the mobility at low values of E/N. Although the results of the previous investigations agree to within the combined stated error limits, the present results appear to be systematically lower than those of James *et al.* (1975) by 2% and Takata (1975) by 1·5% at low values of E/N. Also shown in Fig. 6 are best estimate values of the reduced mobility for K^+ in helium at 80 K from the present work.

The zero field reduced mobility for K^+ ions in helium is shown in Table 3. The value from Creaser (1969) is considered to be subject to significant error due to the presence of charged layers on the Bradbury–Nielsen grids used in this earlier study. For this reason the variation of κ with E/N obtained by Creaser has not been shown in Fig. 6.

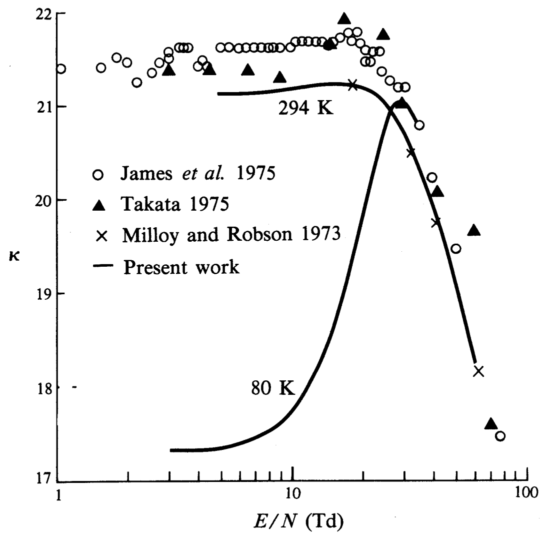


Fig. 6. Reduced mobility of K^+ ions in helium as a function of E/N at room temperature. Results from the present work are shown at both room temperature and 80 K.

Table 3. Comparison of κ_0 values for K^+–He

Authors	T (K)	κ_0	Authors	T (K)	κ_0
Elford and Milloy (1974)	293	$21 \cdot 3 \pm 0 \cdot 2$	Creaser (1969)	77	$18 \cdot 1 \pm 0 \cdot 4$
James *et al.* (1975)	300	$21 \cdot 6 \pm 0 \cdot 4$	Present work	80	$17 \cdot 32 \pm 0 \cdot 26$
Takata (1975)	310	$21 \cdot 4 \pm 0 \cdot 6$			
Present work	294	$21 \cdot 14 \pm 0 \cdot 11$			

(b) Comparison of K^+–Ar Results

The present best estimate values for the reduced mobility of K^+ ions in argon at 295 K are compared with those of previous workers in Fig. 7. The present results agree with those of Milloy and Robson (1973) to within 0·5% and Elford and Milloy (1974) (not shown) to within 0·2% except at 0·0724 kPa where the present results are 0·7% higher at low values of E/N. The results of Takebe *et al.* (1980) agree with the present results to within approximately 0·5% for $E/N > 30$ Td but at low values of E/N they fall below these data. The results of Skullerud (1973) agree with the present results to within the error limits but do not extend to low enough values of E/N to determine the values of the zero field reduced mobility accurately. The results of James *et al.* (1973) are generally higher (by about 1–1·5%) than the present results. The results of Takata (1977) are not shown here due to the large scatter in the data but lie above the results of James *et al.* at values of E/N below 20 Td. Although both of these earlier sets of data agree with the present results to within the error limits, they appear to be systematically higher.

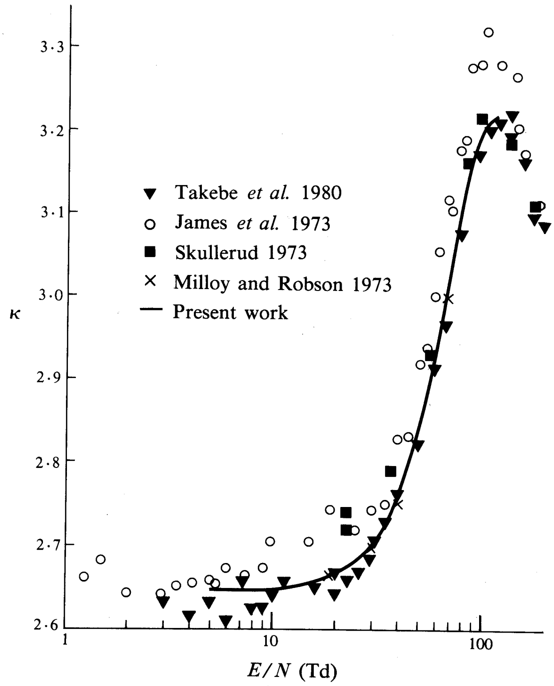


Fig. 7. Reduced mobility of K^+ ions in argon at room temperature.

Table 4. Comparison of κ_0 values for K^+–Ar

Authors	T (K)	κ_0
Tyndall (1938)	291	2·64±0·09
Hoselitz (1941)	291	2·64
Keller *et al.* (1973)	310	2·73±0·06
Milloy and Robson (1973)	293	<2·67±0·05
James *et al.* (1973)	300	2·66±0·05
Elford and Milloy (1974)	293	2·64±0·02
Creaser (1974)	304	2·57±0·03
Takata (1977)	301	2·71±0·09
Takebe *et al.* (1980)	305	2·63±0·03
Present work	295	2·640±0·013

Table 5. Comparison of present κ_0 values with the polarization limit

Ion–gas	T (K)	κ_0 Present	κ_0 Poln limit	Difference (%)
K^+–He	294	21·14±0·5%	16·09	31
	80	17·32±1·5%		8
K^+–Ar	295	2·64±0·5%	2·44	8

Values obtained for the zero field reduced mobility κ_0 are shown in Table 4. When the value of Creaser (1974) on this list is disregarded (because of known systematic errors) it can be seen that with one exception, that of Keller *et al.* (1973), all other values agree to within the stated error limits.

The present values for κ_0 are compared with the polarization limit in Table 5. For both cases investigated it will be necessary to use lower temperatures than those employed in the present work before the measured mobilities are entirely determined by the long range dipole polarization force at low E/N values.

5. Conclusions

The improvement in accuracy of the present data over that available previously and the data at 80 K will enable interaction potentials for K^+ ions in helium and argon to be derived with a smaller error and over a larger range of internuclear separations than has been possible previously.

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