The Mobility of H_3^+ and H_5^+ Ions in Hydrogen and the Equilibrium Constant for the Reaction $H_3^++2H_2 \rightleftharpoons H_5^++H_2$ at Gas Temperatures of 195, 273 and 293 K

M. T. Elford and H. B. Milloy

Electron and Ion Diffusion Unit, Research School of Physical Sciences, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

Abstract

The mobilities of hydrogen ions in hydrogen have been measured by the Bradbury-Nielsen time-offlight method at temperatures of 195, 273 and 293 K, at pressures in the range 0.5-200 torr and at E/N values ranging from 0.4 to 200 Td. The zero field reduced mobilities of H₃⁺ and H₅⁺ have been determined to be $11 \cdot 18 \pm 0.05$ and $10 \cdot 61 \pm 0.05$ cm²s⁻¹V⁻¹ at 293 K, and $11 \cdot 18 \pm 0.05$ and $10 \cdot 53 \pm 0.05$ cm²s⁻¹V⁻¹ at 273 · 2 K respectively. At 194 · 5 K the zero field reduced mobility of H₅⁺ was determined to be $10 \cdot 40 \pm 0.05$ cm²s⁻¹V⁻¹. The thermal equilibrium constant K_e for the reaction H₃⁺ + H₂ + H₂ \rightleftharpoons H₅⁺ + H₂ was obtained by fitting the mobility data as a function of gas pressure. The values of K_e obtained were $1 \cdot 83 \pm 0.45 \times 10^{-18}$, $2 \cdot 8 \pm 0.7 \times 10^{-18}$ and $1 \cdot 6 \pm 0.6 \times 10^{-16}$ cm³ at 293, 273 and 195 K respectively. The reduced mobility of H₃⁺ as a function of E/N was derived for values of E/N up to 200 Td from the data taken at gas pressures less than 2 torr and was found to be in good agreement with the data of Miller *et al.* (1968). The ion species present were identified by the addition of contaminants and by use of supplementary data taken with a drift-tube-mass-spectrometer system. The energy for the dissociation of H₅⁺ into H₃⁺ and H₂ was derived by the method of Eyring *et al.* (1936) and found to be 250 ± 50 meV.

1. Introduction

There have been at least 20 investigations of the mobility of hydrogen ions in hydrogen since the pioneering measurements of N. E. Bradbury in 1932, and this degree of activity reflects the interest in obtaining reliable data for the simplest case of ions moving in their parent diatomic gas. The earlier measurements, i.e. prior to 1960 (Bradbury 1932; J. H. Mitchell, quoted in Tyndall 1938; Bennett 1940; Bennett and Thomas 1942; Lauer 1952) were subject either to effects arising from gas impurities or were made by indirect (i.e. not time-of-flight) methods and were thus liable to serious error. From 1960 to 1965 time-of-flight methods were used in almost all investigations but the reported results (Frommhold 1960; Chanin 1961; Bouciqué and Mortier 1964; Sinnott 1964; Dutton et al. 1966; Skullerud 1966) are conflicting. The first mobility measurements in which the hydrogen ions were positively identified were made by Saporoschenko (1965). Three ion species H^+ , H_3^+ and H_5^+ were observed but the scatter in the experimental data was large. Data of higher accuracy for the mobilities of mass identified H^+ and H_3^+ ions over a wide E/N range (E is the electric field strength and N the gas number density) at room temperature have been reported in a series of papers by the group at the Georgia Institute of Technology (Albritton et al. 1968; Miller et al. 1968; Graham et al. 1973). Low gas pressures were used in this work, and this precluded measurements of the mobility of H_5^+ ions which are the dominant species at much higher gas pressures. Saporoschenko

has shown that H_5^+ ions are produced in three-body reactions with hydrogen molecules. Since the H_5^+ ions may be dissociated in two-body collisions to form H_3^+ , the two-way reaction scheme is represented by

$$H_3^+ + H_2 + H_2 \rightleftharpoons H_5^+ + H_2.$$
 (1)

The only mobility measurements available for H_5^+ ions are those of Saporoschenko (1965), Dutton *et al.* (1966) and Hackam *et al.* (1973), but these three sets of data disagree by up to 25%. Moreover these measurements were all made at relatively low gas pressures and the reduced mobility data were not shown to be independent of pressure. If the reactions (1) are in equilibrium over the whole drift length, the measured reduced mobility κ will be related to the reduced mobilities κ_1 and κ_2 of H_3^+ and H_5^+ respectively by the relation

$$\kappa = (\kappa_1 + K_e p \kappa_2) / (1 + K_e p), \qquad (2)$$

where K_e is the equilibrium constant and p is the gas pressure. It can be seen from equation (2) that, unless the measured reduced mobility can be demonstrated to be independent of pressure, it will not be that of either ion but will correspond to a weighted average of the reduced mobilities of H_3^+ and H_5^+ ions, the weighting depending on the gas pressure.

The major aim of the present work was to measure the reduced mobility over a wide range of gas pressures and to use the relation (2) to derive the reduced mobilities of H_3^+ and H_5^+ as well as the equilibrium constant. Although in principle the relation (2) can be fitted to the data at any value of E/N, because of experimental limitations a sufficiently wide pressure range could be attained only at low values of E/N where the reduced mobility is independent of E/N. The values of the reduced mobilities obtained from the relation (2) under these conditions are therefore zero field reduced mobilities κ_0 , and the equilibrium constants are those corresponding to thermal equilibrium.

Measurements were made at three gas temperatures 194.5, 273.2 and 293 K to enable the dissociation energy of H_5^+ to be derived from the variation of K_e with gas temperature T. There have been a number of theoretical studies of the structure and binding energy of H_5^+ (Huang *et al.* 1972 and references therein) and the experimentally determined dissociation energy is therefore of considerable interest. The variation of κ_0 with T for H_3^+ and H_5^+ is also of theoretical interest although there is at present no satisfactory ion mobility theory for polyatomic ions in diatomic gases.

If small traces of certain impurities are present, a number of ion-molecule reactions involving proton transfer can lead to changes in ion identity and hence to changes in mobility. Much of the early data are thought to be subject to this problem, and in one investigation by Fleming *et al.* (1969) it was suggested that the presence of water vapour, resulting in the formation of H_3O^+ ions, was a possible cause of some of the discrepancies between the earlier measurements. In the present work the investigation of the effects of impurities has been extended to methane, oxygen and nitrogen. The identities of the ions were established by various test procedures such as adding small quantities of selected contaminants, and by the use of a separate drift-tube-massspectrometer apparatus (a description of which we are preparing for publication).

2. Experimental Details and Hydrogen Ion Reactions

The drift velocities of the ions were measured using the Bradbury-Nielsen time-offlight method. The experimental tube employed in the present work was, with one



Fig. 1. Schematic diagram of the ion source and upper section of the electrode system of the experimental tube: A is the cylindrical volume defined by the open cylinder B containing an Americium-241 foil, C and D are electrodes supporting high-transparency meshes, and E is the electrode through which the ions enter the drift space.

modification, identical to that used by Crompton et al. (1970) and Elford and Rees (1974). The experimental technique has been described in detail by Elford (1972) and is not discussed further here. The above-mentioned modification to the experimental tube was the replacement of the electron source, in which the electrons were produced by α -particle ionization alone, by a source of the type described by Crompton and Elford (1973). This source and the region of the electrode system before the first grid of the Bradbury-Nielsen system are shown in Fig. 1. Electrons are produced in region A in ionizing collisions by *a*-particles emitted from an Americium-241 foil wrapped inside the cylinder B. The electrons are extracted from the cylinder by a small extraction field, and they pass through a high-transparency gauze C into a region of very high electric field between gauze C and a similar high-transparency gauze D 1 mm apart. Potential differences of up to 200 V could be applied between C and D with the present equipment. At pressures of less than ~ 10 torr, a Townsend avalanche is produced in the region CD and the number of electrons is considerably increased. Some of the electrons pass through gauze D and produce positive ions from ground state hydrogen molecules in the following ways:

$$e + H_2 \rightarrow H_2^+(^2\Sigma_g^+) + 2e$$
, threshold = 15.6 eV; (3)

$$e + H_2 \rightarrow H_2^+(^2\Sigma_g^+) + 2e \rightarrow H + H^+ + 2e,$$
 18 eV; (4)

$$e + H_2 \rightarrow H_2^+(^2\Sigma_u^+) + 2e \rightarrow H + H^+ + 2e,$$
 28 eV. (5)

The cross section for the reaction (4) is small as it is in violation of the Franck-Condon principle and its value has been estimated by Dunn (1966) to be $\sim 3\%$ of the cross section for the reaction (3). The cross section for the reaction (5) has been shown by Rapp *et al.* (1965) never to exceed 6% of the total ionization cross section. It follows that at low pressures $\sim 95\%$ of the ions formed by electron impact are H_2^+ . At pressures greater than ~ 10 torr, electrons could not be accelerated to the threshold energies for ionization, and the ions were formed solely by α -particle impact. The cross sections for the formation of H^+ and H_2^+ ions under these conditions are not known, but it seems likely that both these ions were formed.

The ions formed in the source undergo the following reactions in addition to (1):

$$H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2, \qquad H_3^+ + H_2 \rightarrow H^+ + H_2 + H_2,$$
 (6a, b)

$$H_2^+ + H_2 \to H_2 + H_2^+, \quad H_2^+ + H_2 \to H_3^+ + H.$$
 (6c, d)

At values of E/N < 90 Td Albritton *et al.* (1968) have shown that the reaction (6b) is insignificant, and this reaction was therefore neglected in the present work. The rate for the reaction (6d) is very large (Ryan and Futrell 1965), and it can be shown that at E/N = 4 Td and a gas pressure of 1 torr (the lowest pressure used in the analysis based on equation 2) less than 1% of the H_2^+ ions remain unreacted after drifting 2 mm in the direction of the field.

The number of H^+ ions which enter the drift section is also insignificant at all pressures. It has already been noted that at low pressures very few protons are produced in the source, and it can be shown using the rate constant for the reaction (6a) (Miller *et al.* 1968) that at higher pressures almost all the protons are converted to H_3^+ ions before the first shutter. Thus at the first shutter the ion population consists of the two species H_3^+ and H_5^+ , the relative proportions of which depend on the rate coefficients for the reactions (1), on the gas pressure and temperature, and on the value of E/N. Since variation of the E/N value in the region DE produced no observable change in the measured mobility, it can be assumed that the reactions (1) were in equilibrium throughout the whole of the drift distance and that the measured mobilities are related to the mobilities of H_3^+ and H_5^+ by equation (2).

The hydrogen was purified by passage through a heated silver-palladium tube. This purification procedure was found to introduce trace amounts of methane and to lead to the production of an impurity ion species. The identification of the methane and its effect on the measurements are discussed in Section 3 below. For the measurements at 195 K, the experimental tube was immersed to just below the level of the tungsten seals in a dry-ice-methyl-alcohol slush bath. The bath temperature was measured by a copper-constant thermocouple calibrated against the sublimation point of solid CO₂, observing the usual precautions at this fixed point (Scott 1959). The gas temperature measurements of $194 \cdot 5$, $273 \cdot 2$ and 293 K are considered to be in error by less than 0.1 K. Throughout the present paper, all values for reduced mobilities κ are quoted in units of cm² s⁻¹ V⁻¹.

3. Identification of Ion Species

Considerable care is required to ensure that the ions whose mobilities are measured are in fact hydrogen ions and not products of reactions of hydrogen ions and impurities. In the present work the identity of the ion species was first investigated by observing the effects of repeated flushing of hydrogen samples through the experimental tube, by observing any changes in the ion-current-shutter-frequency spectrum with time, and by the addition or removal of impurities. These tests are described in subsection a below. The identities obtained in this way were confirmed by the use of a drift-tube-mass-spectrometer system (referred to in the Introduction above) to analyse the ions present under conditions of pressure and E/N identical to some of those used in the experimental tube. The results obtained in these analyses are described in subsection b below.

(a) Ion Species Present in Static Gas Drift Tube

Five different sets of ion current maxima were observed in the ion-current-shutterfrequency plots obtained in the present work. One of these sets of maxima (denoted A) is considered to be due to hydrogen ions subject to the equilibrium reaction $H_3^+ + H_2 \rightleftharpoons H_5^+$ since, except at very high gas pressures, this set of maxima was the only one present in the plots under conditions of maximum gas purity. The mobility data derived from the maxima A were highly reproducible (to within $\pm 0.1\%$ at pressures greater than 2 torr) and the maxima showed no significant asymmetry to indicate the presence of nonequilibrium reactions. At pressures less than 2 torr the resolution and zero stability of the pressure gauge made it impossible to reproduce the data to better than $\pm 0.3\%$. The remaining sets of maxima (denoted B, C, D and E) were all shown to be due to ion species produced by reactions of hydrogen ions with impurities. The species are designated B, C, D and E corresponding to their respective sets of maxima. Only species B gave rise to significant difficulties in the present work.



Fig. 2. Ion-current-shutter-frequency plots for positive ions in hydrogen that had been purified by passage through a silver-palladium thimble operated at the indicated temperatures T_p . The experimental conditions were $p_{273.2} = 71.8$ torr, E/N = 1.13 Td and T = 293 K.

The abundance of species B was found to be virtually unchanged by liquid nitrogen trapping, and was independent of the time the gas was held in the experimental tube, indicating that outgassing was not responsible. By adding small amounts of N_2 and O_2 it was demonstrated that species B was unrelated to either of these contaminants. However, the abundance of species B was found to be strongly dependent on the operating temperature of the silver-palladium tube used to purify the hydrogen. Fig. 2 shows ion-current-shutter-frequency plots for hydrogen samples purified by passage through the silver-palladium tube but at two different tube temperatures 380°C and 130°C. None of the 200 data points taken for each of the curves have been shown as they all lie within the thickness of the lines. The most likely contaminant responsible for species B is methane, the hydrogen combining catalytically with carbon, which is probably present as an impurity in the silver-palladium tube. The ion species B is almost certainly CH_5^+ produced by proton transfer from a hydrogen ion species. An attempt was made to determine the level of methane responsible for the observed level of species B by admitting large quantities of hydrogen into the system via the silver-palladium tube and then removing the hydrogen by surrounding the silver-palladium tube with pure nitrogen. A measurement of the residual gas pressure in the system showed that the methane level was significantly less than 1 p.p.m. As Fig. 2 shows, a considerable reduction in the level of methane, and hence in the abundance of species B, was effected by operating the silver-palladium tube at much lower temperatures even though the time to let in the high pressure gas samples became very long. Despite these precautions, however, the presence of species B became the upper limiting factor to the usable pressure range. Ion species B has a zero field reduced mobility of 11.80, and at pressures in excess of 200 torr the maxima due to this species caused sufficient distortion of the maxima due to species A to prevent accurate measurements being made on the species A maxima.

Species C and D were observed only in preliminary measurements and were reduced in abundance to a negligible level by flushing with hydrogen and by pumping. Species C is a cluster ion formed from a noncondensible impurity (i.e. an impurity which was not removable by a liquid nitrogen trap) and has a reduced zero field mobility κ_0 of 10.49 independent of gas pressure, indicating that it did not undergo reactions in transit but was formed before the first shutter grid. Species D is also a cluster ion formed from a condensible impurity, the reduced mobility at $p_{273,2} =$ 9.56 torr and E/N = 8.45 Td being 11.16. Species E was observed only when significant quantities (~20 p.p.m.) of N_2 were added to the hydrogen sample and it had a reduced mobility of 12.19 at $p_{273.2} = 9.39$ torr and E/N = 8.48 Td. The mobilities of the ion species C, D and E are of minor significance since the identities of the species have not been established, but the small differences between their mobilities indicates the necessity for high resolution and low experimental scatter in hydrogen ion mobility measurements in hydrogen. It is of interest to note that none of the four impurity ion species observed in this work would appear to be H_3O^+ , the ion species investigated by Fleming *et al.* (1969). Only one species (species D) was found to be related to a condensible gas impurity, but its measured mobility is significantly lower than that reported by Fleming et al. for H_3O^+ ions. The nonobservance of an ion having such a mobility is consistent with the very low level of water vapour in the experimental tube.

(b) Investigations with Drift-tube-Mass-spectrometer System

The drift-tube-mass-spectrometer apparatus was used at 293 and 195 K to help identify the ion species present in the drift tube operated under static gas conditions and to estimate the equilibrium constant for the reaction (1). The ion sources used in both drift tubes were identical and the same silver-palladium hydrogen purification system was used in both cases.

At 293 K the most abundant ion species (Fig. 3a) were at 3 a.m.u. (H_3^+) and 5 a.m.u. (H_5^+) but ions were also observed at 17, 19 and 29 a.m.u. As described in subsection a above, the ions at 17 a.m.u. were formed in a reaction between the hydrogen ions and methane molecules produced in the hydrogen purification system.

The identity of the 17 a.m.u. ions (CH_5^+) was established by noting the presence of a peak at 22 a.m.u. (CD_5^+) when deuterium was passed through the thimble (Fig. 3b). It can be seen that the peak at 29 a.m.u. (HN_2^+) has been changed to 30 a.m.u. (DN_2^+) and that the peak at 19 a.m.u. (H_3O^+) has been changed to 20 a.m.u. $(DH_2O^+;$ not D_3O^+ , since H_3O^+ was formed from water vapour present from outgassing of the drift tube walls). The small peaks at 5, 9 and 21 a.m.u. in the deuterium spectrum are due to small quantities of hydrogen desorbed from the palladium when the deuterium was admitted. When the palladium tube was operated at reduced heater power, the CH_5^+ and CD_5^+ peaks were reduced to trace amounts.



Fig. 3. Mass spectrometer traces showing the ion species present and their relative abundances in (a) hydrogen and (b) deuterium at a pressure of $p_{273.2} = 8$ torr, E/N = 2.7 Td and a gas temperature of 293 K. Both gas samples were purified by passage through the same silver-palladium thimble operated at 380°C. The ionic weights (in a.m.u.) of the species are indicated above their associated peaks.

At 293 K the ratio of the H_5^+ peak to the H_3^+ peak was found to increase linearly with pressure over the whole range investigated (3–11 torr) and the equilibrium constant was estimated to be $1 \cdot 3 \times 10^{-18}$ cm³. It is difficult to estimate the error in this value. The most likely source of error is mass discrimination in the quadrupole mass spectrometer. Since the value of the equilibrium constant was independent of pressure, it is thought unlikely that a significant error was introduced by mass discrimination effects at the sampling aperture.

At 195 K the equilibrium constant for the reaction (1) was found to be approximately 3×10^{-16} cm³. However, there was evidence of large mass discrimination errors at the sampling aperture, and for this reason the quoted value should be treated as a rough estimate. At 195 K the H₇⁺ ion was observed, but the low abundance of this ion species (0.1% of H₅⁺ abundance at $p_{273.2} = 7$ torr) makes it very unlikely that this ion would be observed in any of the experiments with the drift tube operated under static gas conditions.

The results of these tests with the drift-tube-mass-spectrometer system confirm that the maxima A correspond to ions undergoing reactions $H_3^+ + H_2 \rightleftharpoons H_5^+$ and that the ion species B is CH_5^+ .

4. Experimental Results

The reduced mobility κ is obtained from the ionic drift velocity W by the relation

$$\kappa = \frac{W}{760 \, E/p_{273\cdot 2}} = \frac{273\cdot 2 \, W p_{\rm T}}{760 \, ET}.$$

	The uni	its are:	E/p_{273}	(V cm ⁻	¹ torr ⁻	¹), E/I	N (Td),	к (сі	$n^{2} s^{-1}$	V ⁻¹),	<i>p</i> ₂₇₃ (t	orr)	
E p _{273.2}	E N	0.926	1.679	2.885	5.03	9.33	к at p ₂₇₃ 14·33	.2 of: 37·4	55.9	71.8	93.7	143.6	186.6
					((a) 293 I	ĸ						
0.15	0.4242					., _, .	-						10.65
0.20	0.5657											10.67	
0.30	0.8485								10.73		10.69		
0.40	1.131							10.78	10.72	10.71			
0.70	1.020							10.79	10.72				
0.70	2.121						10.92	10.78					
1.00	2.828					10.97	10.91	10 /0					
1.50	4.242						10.92						
$2 \cdot 00$	5.657				11.04	10.97	10.91						
3.00	8.485			11.09	11.03	10.96							
4 · 00	11.313			11.09	11.03								
5.00	14.142	11.10		11 00	11.04								
8.00	16.970	11.16	11 11	11.09	11.04								
Best est	0f Ko	11.14	11.12	11.09	11.04	10.96	10.91	10.78	10.72	10.71	10.69	10.67	10.65
						10 20	10 71	10 70	10 72	10 /1	10 05	10 07	10.02
E p _{273.2}	E/N	1.007	2.480	5.424	10.08	15·50	$\kappa \text{ at } p_{273}$ 20.15	.₂ of: 40·30	60.45	77 • 49	100.7	155.0	201 • 5
					<i>(b</i>)	$273 \cdot 2$	ĸ						
0.15	0.4242				(*)	,							10.55
0.20	0.5657										10.59	10.56	
0.30	0.8485								10.61	10.60	10.59		
0.40	1.131								10.61	10.59			
0.20	1.414								10.61				
0.60	1.697				10.05		10.72	10.66					
1.50	4.747				10.83	10.77	10.72						
2.00	5.657				10.84	10.77	10 /2						
3.00	8.485			10.96									
4.00	11.318		11.06	10.95									
5.00	14 · 142		11.05	10.97									
6.00	16.970	11.14	11.06										
8.00	22.630	11.15	11.00										
15.00	20.200	11.07	11.09										
20.00	42.420	11.63											
25.00	70·710	12.31											
30.00	84.850	13.24											
Best est.	of κ_0	11.14	11.06	10.96	10.84	10.77	10.72	10.66	10.61	10.59	10.59	10.56	10.55
E/p _{273.2}	E/N						κ at p ₂₇₃	.2 of:					
		1.414	3.482	7.619	14.15	21.77	28.30	45.66	84.95	108.9	141.7		
					(c)) 194.5	Κ						
0.15	0.4242										10.41		
0.20	0.5657								10.41	10.40	10.40		
0.30	1.131							10.40	10.40	10.40			
0.50	1.414						10.41	10.40					
0.60	1.697												
1.00	2.828					10.40	10.39						
1.50	4.242				10.40	10.39							
2.00	5.657				10 · 39								
3.00	8.485			10.40									
4.00	11.318		10.43	10.40									
5.00	14.142												
6.00	16·970	10.51	10.43										
8.00	22.030	10.72	10.40										
Deet est	20.200	10.73	10.42	10.40	10.20	10.20	10.20	10.20	10.40	10.40	10.40		
Best est.	$\sigma \kappa_0$	10.49	10.43	10.40	10.33	10.39	10.39	10.39	10.40	10.40	10.40		

Table 1. Reduced mobility derived from maxima A

The quoted E/N values are obtained from the relation $E/N = 2.8283 E/p_{273.2}$ Td. The present values of κ corresponding to maxima A are listed as a function of E/Nand $p_{273.2}$ in Table 1 for (a) 293, (b) 273.2 and (c) 194.5 K. It can be seen from Table 1 that there is a range of E/N values where the measured reduced mobility is independent of E/N at a given pressure. In Table 1a this E/N range is 0.4–23 Td, in Table 1b 0.4–17 Td and in Table 1c the range is 0.4–14 Td. Data taken within these E/N ranges may be considered as referring to the zero field reduced mobility κ_0 .



Fig. 4. Reduced zero field mobility κ_0 of H_3^+ ions in hydrogen at the three indicated gas temperatures.

The best estimate values of κ_0 given in Table 1 were obtained by weighting the data in favour of the values taken at the largest electric field strengths. Such data are less subject to the effects of diffusion and contact potential differences between the shutter grids, although it can be seen that there is no significant evidence for the presence of these effects. The best estimate values of κ_0 are plotted in Fig. 4 as a function of $p_{273\cdot2}$ for the three gas temperatures. Theoretical curves of best fit to the data (obtained from equation 2) are also included. At each gas temperature and for $p_{273\cdot2} > 2$ torr, no best estimate value deviates from the curve by more than $\pm 0.1\%$. The values of κ_1 , κ_2 and K_e obtained from these fits are:

Para	meter	$T = 194 \cdot 5$	273 · 2	293 K
κ_1	(H ₃ ⁺)		$11 \cdot 18 \pm 0 \cdot 05$	$11 \cdot 18 \pm 0 \cdot 05$
κ_2	(H ⁺ ₅)	10.40 ± 0.05	10.53 ± 0.05	10.61 ± 0.05
Ke	(cm ³)	$(1.6 \pm 0.6) \times 10^{-16}$	$(2.8 \pm 0.7) \times 10^{-18}$	$(1 \cdot 83 \pm 0 \cdot 45) \times 10^{-18}$

The quoted errors are the fitting uncertainties plus the systematic error due to the experimental parameters such as pressure, temperature etc. The fitting uncertainties were determined by altering the parameters κ_1 , κ_2 and K_e in equation (2) either singly or in combinations until the calculated curves lay outside the $\pm 0.1\%$ statistical uncertainty. This is a reliable procedure since there is a considerable separation of

the effects of altering the parameters κ_1 , κ_2 and K_e on the calculated curve. An alteration of κ_1 causes an almost identical change in the calculated values of κ_0 at low pressures but a negligible change in the values predicted at very high pressures. A change in K_e causes the calculated curve to be translated along the pressure axis; an increase in K_e causing a translation of the curve towards lower pressures. In the fitting procedure to obtain K_e at 194.5 K, it was necessary to assume a value for the reduced zero field mobility of H_3^+ , as accurate data could not be taken at sufficiently low pressures for the measured mobility to become independent of pressure. The value assumed for κ_1 in this case was 11.18, i.e. the value of κ_1 at 273.2 and 293 K.

	ка	Best est. of		
(Td)	0.504	0.935	2.303	κ
22.63		11.20	11.12	11.20
28.28		11.21	11.14	11.21
33.94		11.25	11.17	11.25
42.42	11.39	11.35	11.28	11.35
50·91	11.57	$11 \cdot 54$	11.48	11.54
56.57	11.78	11.76	11.68	11.76
70.71	12.49	12.45	12.39	12.45
84.85	13.44	13.39	13.32	13.39
113.1	15.08	15.09		15.09
141 • 4	15.84	15.89		15.89
169.7	15.75			15.75
198.0	15.22			15.22

 Table 2.
 Reduced mobility derived from maxima A

Since the zero field mobility for H_3^+ does not alter significantly over the temperature range 273·2–293 K it is expected that, over the range 273·2–194·5 K, the value of κ_0 for H_3^+ would either be constant or at most a slowly varying function. The assumption that κ_0 for H_3^+ is constant with *T* over the range 194·5–293 K is not expected to be greatly in error. However, if the value of κ_0 assumed for H_3^+ at 194·5 K is in error by 1%, the change in K_e is expected to be less than 15%. The uncertainty quoted for K_e at 194·5 K includes a component based on the assumption that the value of κ_0 for H_3^+ at 194·5 K is not more than 1% different from that at 293 K. It should be noted that the value of K_e at 293 K (1·83×10⁻¹⁸ cm³) derived from fitting equation (2) to the reduced mobility data is in reasonable agreement with the value of K_e (1·3×10⁻¹⁸ cm³) obtained at this temperature from measurements of the ratio of the H_3^+ to H_5^+ ion currents using the drift-tube-mass-spectrometer system (see Section 3*b*).

It is apparent from Fig. 4 that mobilities measured at 293 K and at pressures less than 1 torr differ insignificantly from the value of the mobility of H_3^+ ions, and such data may therefore be assumed to refer to this ion species. At values of E/N greater than those referred to in Fig. 4 this assumption becomes less subject to error since the equilibrium constant decreases as E/N increases. Table 2 and Fig. 5 show the best estimate values of the reduced mobility of H_3^+ at 293 K over the E/N range 23–200 Td together with data of Miller *et al.* (1968) for mass-identified H_3^+ ions. Although data at $p_{273} < 1$ torr could not be taken at E/N values less than 23 Td it is apparent from Table 1*a* that the reduced mobility of H_3^+ ions for the E/N range

0.4-23 Td is therefore shown as a broken line. Due to the resolution of the quartz spiral manometer used in these measurements, the uncertainty in κ due to the pressure measurement is estimated to be $\pm 1\%$ at 0.504 and $\pm 0.5\%$ at 0.935 torr. To within these error limits there is no significant dependence on gas pressure up to E/N = 140 Td, suggesting that diffusion errors and other end effects cause errors of less than 1%.



At E/N values greater than 140 Td, only data at one pressure are available and hence it was not possible to check for end effects. The best estimate values are considered to be in error by less than 1% up to E/N = 85 Td and 2% up to E/N = 140 Td. The upper limit to the E/N range was fixed by the onset of a severe (2%) disagreement between the mobility values derived from different maxima in the ion-current – shutterfrequency plots. The cause of this effect is unknown, and it prevented data being taken at E/N values of 300 Td and greater, where the data of Miller *et al.* (1968) show an increase in reduced mobility as E/N increases, although it should be noted that this variation from the curve extrapolated from lower E/N values falls within the error limits stated by Miller *et al.* Over the entire common E/N range the agreement between the present data for H₃⁺ ions and those of Miller *et al.* is very satisfactory. For E/N values between 140 and 200 Td the close agreement indicates that the present data are not subject to serious errors due to end effects.

5. Discussion

The values of κ_0 obtained in the present work for H_3^+ and H_5^+ are compared in Table 3 with measurements of hydrogen ion mobilities made since 1965. The most striking feature is the excellent agreement between the results of all workers since

805

1968 for H^+ and H_3^+ ions. There is therefore little doubt that the values of Saporoschenko (1965) are subject to a systematic error of ~10%. In preparing Table 3 some alternative assignments of ion identity have been made. Skullerud (1966) did not speculate about the identity of the ion species present in his measurements but, from his experimental conditions and the value he obtained, there can be little doubt that

Author	Mass ident-	Ion species*				
	ification	H+	H_3^+	H ₅ +	Other	
Saporoschenko (1965)	YES	14.4	10.2		9·6 ^A	
Dutton et al. (1966)	NO				10.8 ± 0.5^{B}	
Skullerud (1966)	NO		11.1 ± 1^{c}		_	
Albritton et al. (1968)	YES	16.0 ± 0.8	11.1 ± 0.6			
Miller et al. (1968)	YES	15.7 ± 0.6	11.1 ± 0.5			
Fleming et al. (1969)	NO	15.7 ± 0.2	11.0 ± 0.2		12.6 ± 0.2^{D}	
Graham et al. (1973)	YES	16.0 ± 0.3	11.3 ± 0.2			
Hackam et al. (1973)	NO		11.1 ± 0.6		$7 \cdot 0 \pm 0 \cdot 5^{E}$	
Present work	NO		$11\!\cdot\!18\!\pm\!0\!\cdot\!05$	$10\!\cdot\!61\pm0\!\cdot\!05$		

Table 3. Values of κ_0 for hydrogen ions in hydrogen (~293 K)

* Notes on suggested identifications:

^A Stated by the author to be the value for H_s^+ ; however, in view of the pressures used (0.5-1.6 torr) and the present work, it is probable that the H_s^+ ions had spent a significant fraction of their transit time as another ion species.

^B Speculated by the authors to be the value for H_{5}^{+} ; however, in view of the pressures used (0.5–6 torr) and the present work, the measured ions were probably either an impurity species or ions which had spent a significant part of their transit time as another ion species.

^c Identity not suggested by the author but probably H_3^+ .

^D Suggested by the authors to be the reduced zero field mobility of H_3O^+ .

^E Stated by the authors to be the value for H_5^+ ; however, in view of the pressures used (1.5-2.8 torr) and the present work, it is probable that the ions observed had either spent a significant fraction of their transit time as another ion species or were impurity ions.

the ion present was H₃⁺. Although Saporoschenko employed direct mass identification, the gas pressures used by him covered the range 0.5-1.6 torr, and on the basis of the present work the ions he observed as H_5^+ would have spent most of their transit time as H_3^+ . The pressure range was too small and the experimental scatter too large for a dependence of the reduced mobility on pressure to be observed. The small difference of 0.6% which he found between his values for H₃⁺ and H₅⁺ suggests that this explanation is correct. A similar criticism can be made of the values obtained by Dutton et al. (1966) who used pressures from 0.5 to 6 torr, although the quoted error of $\pm 5\%$ covers the whole of the ordinate shown in Fig. 4 and hence no further conclusion can be drawn. The value of Hackam et al. (1973) for H⁺₅ ions appears to be anomalously low and, on the basis of the present data, cannot be explained simply by assuming that the observed ions have spent a fraction of their transit time as H_3^+ ions. Although the most probable explanation of the value of Hackam et al. is that the observed ion was a cluster ion, it cannot be any of the four species of cluster ions observed in the present work nor H₃O⁺ observed by Fleming et al. (1969), since for all these cases the values of κ_0 are very significantly larger than that reported by Hackam et al.

The data available at temperatures below room temperature are confusing. There are no other data available at 273 K but at 195 K there are four other measurements,

none of which were made with direct mass identification. These values of κ_0 at ~195 K are shown in Table 4. Chanin (1961) assumed that the ion measured at 195 K was H₃⁺ but the value he obtained at 300 K was 12.3 and this disagrees with the value of 11.2 which is now well established as being the value for H₃⁺ at ~300 K. Fleming *et al.* (1969) have obtained a value of κ_0 for H₃O⁺ of 12.6, and they have suggested that the ion species measured by Chanin was this ion and not H₃⁺. There is clearly significant doubt concerning the identity of the ion in Chanin's room temperature measurements and it is unprofitable to speculate on the identity of the ions at 195 K in Chanin's measurements.

identifications are those stated by the authors						
Author	κ_0 for ${\rm H_3^+}$	κ_0 for H ⁺ ₅				
Chanin (1961)	13.3					
Bouciqué and Mortier (1964)	13·3 ^A					
Sinnott (1964)	~10					
Hackam et al. (1973)	9.5 ± 0.5	4.5 ± 0.5				
Present work	> 10 · 5	10.40 ± 0.05				

Table 4. Values of κ_0 for hydrogen ions in hydrogen (~195 K) All available values of κ_0 for hydrogen ions in hydrogen at 195 K were obtained in experiments without direct mass identification, and the listed identifications are those stated by the authors

^A Identity not stated by authors.

A similar criticism to that applied to Chanin's (1961) data may be applied to the data of Sinnott (1964). At room temperature Sinnott obtained a value of κ_0 of $10 \cdot 2 \pm 0 \cdot 5$ which he considered may have referred to H_5^+ . On the basis of the present work the ions he measured should have had mobilities lying between $10 \cdot 9$ and $11 \cdot 1$, corresponding to the pressures used by Sinnott, the ions spending part of the transit time as H_3^+ and part as H_5^+ . No pressure dependence was observed by Sinnott, and the difference between his value of $10 \cdot 2$ and that expected on the basis of the present work is outside the sum of the respective experimental errors. These facts suggest that the ions observed by Sinnott at room temperature were an impurity species and hence it follows that the value of 10 which he obtained at 195 K is most probably also that for an impurity species.

Bouciqué and Mortier (1964) derived ion mobilities from the study of ions in a sheath near the central wire of a proportional counter. The technique is indirect and the value of κ_0 obtained at room temperature of 12.4 may be compared with the established value of 16.0 for H⁺ ions and 11.2 for H⁺₃ ions. If it is assumed that the error in Bouciqué and Mortier's value is less than ~10%, it may be concluded that the ion with a zero field reduced mobility of 12.4 is an impurity ion. As a consequence the value of κ_0 reported by Bouciqué and Mortier for hydrogen ions in hydrogen at 195 K is suspect, the ions observed at 195 K being probably impurity ions also.

The data of Hackam *et al.* (1973) for 195 K disagree significantly with the present data. Although no value of κ_0 for H₃⁺ ions at 194.5 K was obtainable in the present work, it has been shown that the value must be greater than 10.5, and this disagrees significantly with the value of Hackam *et al.* of 9.5 ± 0.5 . Their value of κ_0 for H₅⁺ at 195 K is less than half that found in the present work and must be regarded with strong reservations in view of the anomalous dependence of κ on E/N which Hackam *et al.* observed at 195 K for H₅⁺ ions.

6. Derivation of Dissociation Energy of H_5^+

It is possible, as mentioned in the Introduction, to derive the dissociation energy from measurements of the equilibrium constant as a function of gas temperature. The equilibrium constant for the reaction

$$H_3^+ + H_2 \rightleftharpoons H_5^+$$

may be written as (Laidler 1950)

$$K_{\rm e} = (F_5/F_3 F_2) \exp(-D/kT), \tag{7}$$

where F_5 , F_3 and F_2 are the partition functions for the species H_5^+ , H_3^+ and H_2 respectively, and D is the energy required to dissociate H_5^+ into H_3^+ and H_2 . Following Eyring *et al.* (1936), the partition functions for H_5^+ , H_3^+ and H_2 are written as the following products:

$$F_5 = F_5^{t} \cdot F_5^{r} F_5^{v} \cdot F_3^{r} F_3^{v} \cdot F_2^{r} F_2^{v}, \qquad F_3 = F_3^{t} \cdot F_3^{r} F_3^{v}, \qquad F_2 = F_2^{t} \cdot F_2^{r} F_2^{v},$$

where the superscripts t, r and v denote translational, rotational and vibrational contributions to the partition function respectively. The pre-exponential factor in equation (7) thus becomes

$$F_5^{t} F_5^{r} F_5^{v} / F_3^{t} F_2^{t}. \tag{8}$$

Such an expression was used by Eyring *et al.* to derive a value of the equilibrium constant for the clustering of various hydrogen ion species with hydrogen. An analogous expression has been used by Voshall *et al.* (1965) to obtain the energy of dissociation of O_4^- into O_2^- and O_2 . In this latter case it was assumed that there was no vibrational excitation of O_4^- at the temperatures considered. In using the expression (8) for the pre-exponential factor it has been assumed that, when the H₂ and H₃⁺ particles are in the complex H₅⁺, they have the same rotational and vibrational motion as when they are independent particles. The degree of validity of this assumption depends on the structure and binding of the H₅⁺ complex.

The structure of H_5^+ has been the subject of a number of theoretical investigations (e.g. Pfeiffer *et al.* 1967; Poshusta and Matsen 1967; Poshusta *et al.* 1969; Easterfield and Linnett 1970). In the most recent and extensive calculations of Huang *et al.* (1972) it has been proposed that the H_2 is situated about 3 a.u. from the H_3^+ apex and is perpendicular both to the H_3^+ plane and to a line extending from the midpoint of the base of the H_3^+ through the H_3^+ apex and through the H_2 midpoint. The H_2 and H_3^+ particles are therefore identifiable structures within the H_5^+ complex, and it is shown below that they are only loosely bound to each other. A high degree of independent motion may therefore be assumed for the H_2 and H_3^+ particles, and the initial assumption that their rotational and vibrational motions are the same as when the particles are separate seems unlikely to be seriously in error.

Each of the partition functions in the expression (8) has a temperature dependence (Aston and Fritz 1959) and thus the overall temperature dependence of the preexponential factor will depend on the assumptions made concerning the excitation of particular modes of motion. At the temperatures used in the present work, the complex H_5^+ will be excited rotationally but there is doubt concerning the excitation of vibrational motion. If it is assumed that no vibrational excitation of H_5^+ occurs at temperatures in the range 195–293 K, the pre-exponential factor is independent of T. Fig. 6 shows $\ln(K_e)$ plotted as a function of 1/kT. The dissociation energy of 230 ± 30 meV was obtained from the slope of the line of best fit. The error limits of ± 30 meV were derived from the slopes of lines of maximum and minimum slope consistent with the indicated error bars. If one mode of vibration is assumed to occur at temperatures in the range 195–293 K, the pre-exponential factor becomes proportional to T. In this case $\ln(K_e T^{-1})$ was plotted as a function of 1/kT, and a dissociation energy of 250 ± 30 meV was found. The relative insensitivity to the temperature dependence of the pre-exponential factor arises from the relatively large value of the dissociation energy.



Fig. 6. Plot of $\ln(K_e)$ as a function of 1/kT. The slope of the line gives the energy for the dissociation of H_s^+ into H_s^+ and H_2 as 230 ± 30 meV.

The best estimate value of the dissociation energy of H_5^+ into H_3^+ and H_2 is considered to be 250 ± 50 meV, the error limits taking into account the uncertainty in the temperature dependence of the pre-exponential factor. This value is somewhat larger than the value of 185 meV obtained from *ab initio* calculations by Huang *et al.* (1972) but, in view of the assumptions made in deriving the dissociation energy from the relation (7), the two results may be considered to be in good agreement.

7. Conclusions

The majority of the investigations into the mobility of hydrogen ions in hydrogen over the last 10 years have been concerned with the ion species H^+ or H_3^+ , and the zero field reduced mobilities of these ions may now be regarded as being established with good precision. Such investigations were confined to relatively low gas pressures where the formation of significant fractions of H_5^+ ions by the three-body reaction from H_3^+ did not occur. The present study has concentrated on the higher pressure range and is the first to demonstrate the pressure dependence of the reduced mobility which arises from the hydrogen ion species H_3^+ and H_5^+ changing identities many times during their transit of the drift tube. At low gas pressures the data refer to ions which have spent virtually their entire transit time as H_3^+ . The present data taken at low pressures are in excellent agreement with those of Miller *et al.* (1968) over a wide E/N range. At very high gas pressures the present data refer to ions which have spent virtually their entire time as H_5^+ ions. Due to the high gas pressures required, the experimentally accessible range of E/N values was limited to the range of E/N values where the reduced mobility of H_5^+ ions was constant.

The variation of the zero field reduced mobilities with temperature is small for both H_3^+ and H_5^+ . In the case of H_3^+ there was no observable difference caused by a 20 K temperature change from 293 to 273 K, while the H_5^+ value changed by only 2% for a change of ~98 K (i.e. from 194.5 to 293 K).

The accuracy with which the equilibrium constant can be determined depends on the statistical scatter of the data and the difference between the reduced mobilities of the two species. In the present case of the equilibrium reaction $H_3^+ + H_2 \rightleftharpoons H_5^+$, the differences in the reduced mobilities of H_3^+ and H_5^+ are only $5 \cdot 7\%$ at 293 K and $6 \cdot 5\%$ at 273 K over the E/N range where the reduced mobilities are independent of E/N. Even though the statistical scatter is as low as $\pm 0.1\%$ it is not possible to determine K_e with an uncertainty of less than $\pm 25\%$. There seems little likelihood at present of significantly reducing the statistical scatter below 0.1% and thus reducing the error in K_e . The dissociation energy for H_5^+ derived from the variation of K_e with T also reflects the uncertainty in the derivation of K_e . In view of the additional assumptions involved in the expression for the equilibrium constant, the present value of 250 meV may be considered to be in satisfactory agreement with the most recent value of 185 meV obtained from *ab initio* calculations by Huang *et al.* (1972) of the structure of H_5^+ .

Finally, the effects of small traces of impurity in the gas samples used should be noted. Many of the earlier hydrogen ion mobility data are considered to be invalid for this reason. When data are taken at high gas pressures, the presence of trace levels of impurities becomes particularly significant, the hydrogen ion species undergoing rapid conversion to ion species involving the impurity molecule. The hydrogen purification procedure, however, may itself introduce gaseous impurities and, in the present work where the purification was performed by passing hydrogen through silver-palladium, trace levels of methane were introduced. Care had to be taken to keep the production of this impurity, and hence the abundance of CH_5^+ ions in the experimental tube, to a minimum.

Acknowledgment

We wish to thank Dr R. W. Crompton for his comments on this paper and for bringing the question of hydrogen ion mobility measurements to our attention.

References

Albritton, D. L., Miller, T. M., Martin, D. W., and McDaniel, E. W. (1968). Phys. Rev. 171, 94.
Aston, J. G., and Fritz, J. J. (1959). 'Thermodynamics and Statistical Thermodynamics' (Wiley: New York).

Bennett, W. H. (1940). Phys. Rev. 58, 992.

Bennett, W. H., and Thomas, L. H. (1942). Phys. Rev. 62, 41.

Bouciqué, R., and Mortier, P. (1964). Bull. Soc. Belge Phys. (4), No. 2, 93.

Bradbury, N. E. (1932). Phys. Rev. 40, 508.

Chanin, L. M. (1961). Phys. Rev. 123, 526.

Crompton, R. W., and Elford, M. T. (1973). Aust. J. Phys. 26, 771.

Crompton, R. W., Elford, M. T., and Robertson, A. G. (1970). Aust. J. Phys. 23, 667.

Dunn, G. H. (1966). J. Chem. Phys. 44, 2592.

Dutton, J., Llewellyn-Jones, F., Rees, W. D., and Williams, E. M. (1966). Phil. Trans. Roy. Soc. London A 259, 339.

Easterfield, J., and Linnett, J. W. (1970). Chem. Comm. p. 64.

Elford, M. T. (1972). 'Case Studies in Atomic Collision Physics', Vol. 2, Ch. 2 (North-Holland: Amsterdam).

Elford, M. T., and Rees, J. A. (1974). Aust. J. Phys. 27, 333.

Eyring, H., Hirschfelder, J. O., and Taylor, H. S. (1936). J. Chem. Phys. 4, 479.

Fleming, I. A., Tunnicliffe, R. J., and Rees, J. A. (1969). J. Phys. B 2, 780.

Frommhold, L. (1960). Z. Physik 160, 554.

Graham, E., James, D. R., Keever, W. C., Albritton, D. L., and McDaniel, E. W. (1973). J. Chem. Phys. 59, 3477.

Hackam, R., Chaudry, J. I., and Mellor, D. J. (1973). Proc. 11th Int. Conf. on Phenomena in Ionized Gases, Prague, 1973, p. 5.

Huang, J. J., Schwartz, M. E., and Pfeiffer, G. V. (1972). J. Chem. Phys. 56, 755.

Laidler, K. J. (1950). 'Chemical Kinetics' (McGraw-Hill: New York).

Lauer, E. J. (1952). J. Appl. Phys. 23, 300.

Miller, T. M., Moseley, J. T., Martin, D. W., and McDaniel, E. W. (1968). Phys. Rev. 173, 115.

Pfeiffer, G. V., Huff, N. T., Greenawalt, E. M., and Ellison, F. O. (1967). J. Chem. Phys. 46, 821.

Poshusta, R. D., Haugen, J. A., and Zetik, D. F. (1969). J. Chem. Phys. 51, 3343.

Poshusta, R. D., and Matsen, F. A. (1967). J. Chem. Phys. 47, 4795.

Rapp, D., Englander-Golden, P., and Briglia, D. D. (1965). J. Chem. Phys. 42, 4081.

Ryan, K. R., and Futrell, J. H. (1965). J. Chem. Phys. 42, 824.

Saporoschenko, M. (1965). Phys. Rev. 139, A349.

Scott, R. B. (1959). 'Cryogenic Engineering' (Van Nostrand: Princeton, N. J.).

Sinnott, G. (1964). Phys. Rev. 136, A370.

Skullerud, H. R. (1966). Proc. 7th Int. Conf. on Phenomena in Ionized Gases, Belgrade, 1965, Vol. 1, p. 50 (Gradevinska Knjiga Publishing House: Belgrade).

Tyndall, A. M. (1938). 'The Mobility of Positive Ions in Gases' (Cambridge Univ. Press).

Voshall, R. E., Pack, J. L., and Phelps, A. V. (1965). J. Chem. Phys. 43, 1990.

Manuscript received 1 July 1974

