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Mobilities of Li^+ ions in H_2, N_2, and their mixture

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The mobilities of Li^+ ions in H_2 and N_2 gases have been measured at (26–38) °C gas temperature over a range of E/N, the ratio of electric drift field to the gas number density, from 8 to 280 Td (1 Td = 10^{-17} V cm^2). The zero-field reduced mobilities were measured to be 12.3 and 4.1 cm^2/V sec in H_2 and N_2 gases, respectively. It was found that the mobility in N_2 gas decreases monotonically down to a value 3.7 cm^2/V sec below 90 Td with an increase in E/N, and thereafter increases. The mobilities of Li^+ in mixtures of H_2 and N_2 gases have been measured at E/N = 15, 31, 93, and 173 Td. A slight deviation from Blanc's law is noticed at E/N = 173 Td. A simple numerical method to obtain the mobility in mixture gases is proposed.

I. INTRODUCTION

According to Blanc's law, the reciprocal of the mobility of an ion moving in a gas mixture varies linearly with the fractional concentration of constituent gases. Many experimental results on mobility at very low E/N (where E is drift field and N the neutral-gas number density) show that this is true unless the ions form clusters with the constituent gas molecules or with impurities.[1-5] Theoretical investigations on the deviation of mobility from Blanc's law at low E/N have been described in the literature.[6,7]

Milloy and Robson[8] were the first to present evidence for the deviation from Blanc's law. They also developed an equation to explain this deviation. However, their theory is applicable only in case where the mobility is a slowly-varying function of E/N and no inelastic scattering occurs. Mason and Hahn[9] have derived an equation which predicts the mobility in gas mixtures at arbitrary field strengths, but in their derivation it has been assumed that cross sections of the collision of an ion with gas molecules are constant. This is not correct in general. Very recently, Whealton and Mason[10] obtained, by correcting improper expressions in their earlier paper,[9] the same equation as that of Ref. 8.

In the present work, the mobilities of Li^+ in H_2 and N_2 gases and their mixtures were measured with the drift-tube mass-spectrometer method. The mobility changes rapidly with E/N at large E/N. A simple numerical method is proposed which enables us to obtain the mobility in gas mixtures over a wide range of E/N values.

II. EXPERIMENTAL METHOD

The apparatus used in this work is similar to that of Miller and his co-workers.[11] A brief description will be given below. Figure 1 shows the vacuum and gas inlet systems schematically. The whole system except the gas reservoir was evacuated to a pressure less than 5×10^{-9} Torr with a 1200-liter/sec diffusion pump after bakeout for 15 h at 250 °C. The pressure of the system was still less than 2.5×10^{-5} Torr one hour after closing the valve in front of the diffusion pump. The gas reservoir was evacuated to a pressure less than 2×10^{-8} Torr with a 20-liter/sec ion pump. H_2 and N_2 gases were mixed in the reservoir and admitted into the chamber through an automatic pressure controller (Granville Philips Series 213) connected to a capacitance pressure meter (MKS Baratron type 90H-30). The purities of the H_2 and N_2 gases were better than 99.999% each, and no attempt has been made at further purification.

The drift tube consists of 14 gold-plated guard rings connected with bakable resistors of 30 kΩ and has an inner radius of 100 mm and a height of 430 mm. The electric field distortion in this drift tube was calculated[12] to be less than 0.07% in the region where the radius is less than 60 mm. Although the ion source can be adjusted to any position in the drift tube, only three stages of the guard rings were used in this experiment for reduction of the measuring time. Accordingly, the corresponding ion drift lengths were 30, 60, and 90 mm.

Following the method reported by Allison and Kamegai[13] β-eucryptite was prepared for the lithium ion emitter. The platinum mesh filament coated with the β-eucryptite was employed for the lithium ion source. Ion bursts of a few microseconds width are periodically gated out of the source into the drift region by a double-grid electric shutter. A mass spectrometer (EAI QUAD 150) was set to select only $^7Li^+$. Detection was made with an electron multiplier. The signals were stored in a 256-channel high-speed time analyzer.[14] The mobility was obtained from the differences between the mean arrival times derived from the time spectra for three different ion source positions. The procedure mentioned above, called the differencing method, eliminates the effect of the period of time required for ions moving outside the drift tube, and the end effects in either the source or exit region of the drift tube. The influence of the diffusion on mobility is also eliminated by this method.[11]

The reduced mobility was derived from the mobility obtained by the method mentioned above by correcting for gas temperature. The temperature was assumed to be equal to the average temperature measured near the exit plate of the ion source and at four different positions outside the drift tube. The temperature was (31–48)°C near the exit plate and (19–38)°C at the drift tube. The average temperature was usually in the range between 26 and 38 °C.

Diameters of the exit apertures of the ground plate of the drift tube and the skimmer are 0.4 mm each. With this dimension, the gas flow at the exit aperture is the medium flow, which is the transition mode from viscous to molecular flow, for gas pressures used in this experiment. In the case of medium or molecular flow, the flow rate of each gas component of the mixture is not always the same. Therefore, the mixing ratio of the gas mixture in the drift tube varies with time.[15] There is no simple experimental method available to determine the mixing ratio of the gas in the drift tube. However, a simple calculation, assuming the flow at the exit aperture to be of the type of the molecular flow, implies that the mixing ratio of the gas mixture in the drift tube settles upon a constant value for each gas of different mixture ratio after the gas is injected for at least one hour. Therefore, measurements were made at least one hour after the injection of the gas mixture was started. Measurements in the mixture were taken at a fixed pressure of 0.4 Torr and at $E/N = 93$, 173, 31, 15, and again 93 Td for the gases of various mixing ratios.

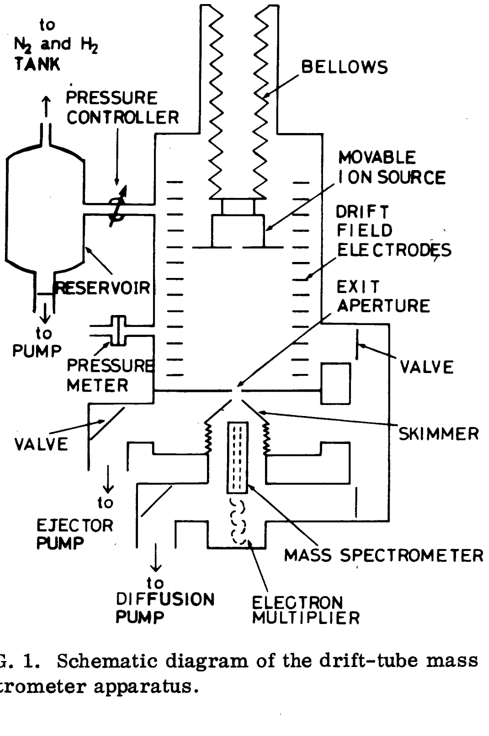

FIG. 1. Schematic diagram of the drift-tube mass spectrometer apparatus.

III. EXPERIMENTAL RESULTS

The mobilities of Li^+ were measured at gas pressures of 0.3 to 0.8 Torr for H_2 and 0.38 to 2.2 Torr for N_2. Figure 2 shows the plot of the reduced mobility of Li^+ in H_2 gas. The value of the zero-field reduced mobility 12.3 $cm^2/V\,sec$ was obtained. The solid curve indicates the result of Miller and his co-workers.[11] A value 12.5 $cm^2/V\,sec$ for the zero-field reduced mobility has been reported by Bristol group.[16] Langevin's theory gives a zero-field reduced mobility of 12.47 $cm^2/V\,sec$. The present result agrees well with these values.

Figure 3 shows the reduced mobility of Li^+ in N_2 gas. No experimental data have been reported so far except that by Mitchell and Ridler[17] shown by the solid line. A value 4.4 $cm^2/V\,sec$ is obtained for the zero-field reduced mobility with Langevin's theory. Mitchell and his co-workers did not use a mass analyzer. However, since the abundance of ^6Li is only 7.4% of Li, the influence of $^6Li^+$ on the mobility of $^7Li^+$ in N_2 gas is estimated to be only 0.5% or less.

The present result shows that the mobility of Li^+

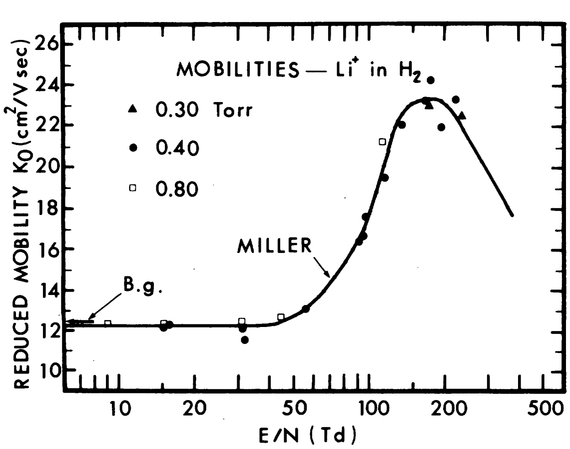

FIG. 2. Comparison of the reduced mobilities for Li^+ ions in hydrogen with the results of Miller *et al.* (see Ref. 11) and the result of Bristol group (see Ref. 16).

in N_2 gas decreases slightly in the range below 90 Td with an increase of E/N, and thereafter increases. It is shown in Fig. 4 that even in the mixture of H_2 and N_2, the mobility of Li^+ at $E/N = 93$ Td is lower than that at a smaller value of E/N when the mixture is abundant in N_2.

When some ions disappear through clustering reaction, the mean drift velocity is measured to be somewhat larger than the "true drift velocity." This is because the ions arriving later have more chances to form clusters which are discriminated by the mass analyzer. The increase of the velocity due to the effect is about $2\alpha D_L/V_d^2$ where α is the frequency of the ion loss, D_L the longitudinal diffusion coefficient, and V_d the "true drift velocity."[18] For low E/N, the longitudinal diffusion coefficient is given by the Einstein relation

$$D_L = V_d kT/eE \, . \tag{1}$$

Here e is the ionic charge, E is the electric field strength, k is Boltzmann's constant, and T is the gas temperature. In order to estimate the value α, we might assume an upper bound of 10^{-29} cm^6/sec on $C(=\alpha/N^2)$, the constant of the clustering reaction of Li^+ with N_2 molecule where N is the number density of N_2 molecule.[19, 20] If we assume that the reduced mobility of Li^+ ions is 4 cm^2/V sec, the increase of the velocity is less than 2% at $E/N = 10$ Td for N_2 gas at 1 Torr, and the increase diminishes rapidly with an increase of E/N.

On the other hand, there is some possibility that clusters once formed dissociate, resulting in the ions and molecules. This process would make the drift velocity of the ion smaller. Figure 5 shows the current variations with E/N for Li^+, $Li^+ \cdot N_2$, and $Li^+ \cdot H_2O$ on the electron multiplier when the N_2 gas is at 1 Torr and the drift length is 90 mm. The dotted line in the figure indicates the ratio of the current of $Li^+ \cdot N_2$ to that of Li^+. The current ratio of $Li^+ \cdot H_2O$ to Li^+ was 0.0175 at 23 Td. The mobility of the cluster $Li^+ \cdot N_2$ gas was not measured, but can be roughly estimated from the relation that the mobility of an ion in the gas is inversely proportional to the square root of the reduced mass of the ion-molecule system. Therefore, if clustering and dissociating reactions were in an equilibrium, the mobility decreases in value by $0.45X/(1+X)$ where X is the current ratio of the cluster to the ion. The decrease of the mobility was estimated to be 6% at 25 Td, 3% at 53 Td, and 1% at 75 Td from the current ratio in Fig. 5. In this estimation, no correction was made owing to the difference between the transverse diffusion coefficients of Li^+ and $Li^+ \cdot N_2$. Exactly speaking, this experiment is not in the equilibrium condition. This means that the above values are overestimated.

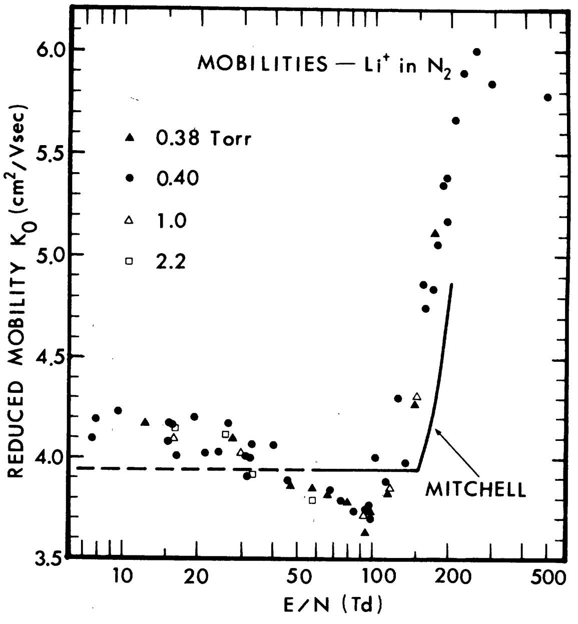

FIG. 3. Comparison of the reduced mobilities for Li^+ ions in nitrogen with the results of Mitchell and Ridler (see Ref. 17).

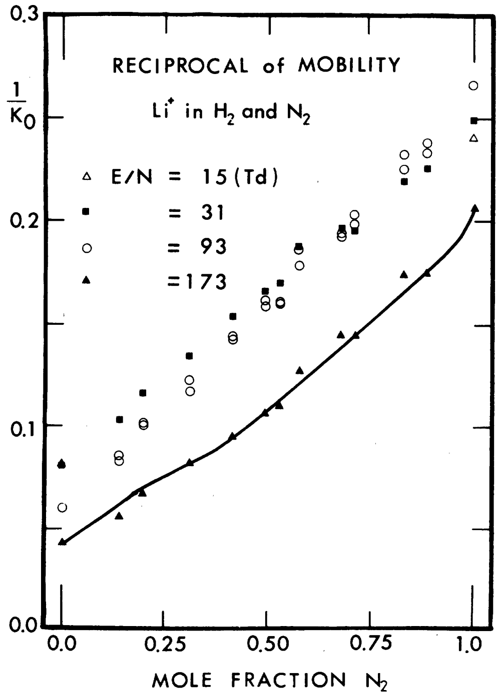

FIG. 4. Reciprocal mobilities of Li^+ ions in gas mixtures of H_2 and N_2 at different values of E/N. The values of reciprocal mobilities for various mixtures at $E/N = 15$ Td are assumed to be on a straight line passing the two points corresponding to the pure gases. Solid line, result of calculation for $E/N = 173$ Td.

Every mobility of the alkali-metal ion reported so far except one,[21] shows monotonic increase with *E/N* until the peak of a bump at high *E/N*. The small decrease of mobility with *E/N* in Ref. 21 was explained in terms of diffusion effects and reversible clustering reactions.[22] In the present result in N_2 gas, there was an initial decrease of the reduced mobility with increasing *E/N*, followed by an increase. The zero-field reduced mobility was measured to be 4.1 $cm^2/V\,sec$. This is the value which is not corrected owing to the effects of the reversible clustering reactions. A minimum value of the mobility, 3.7 $cm^2/V\,sec$, was obtained at 90 Td. The initial decrease seems unable to be explained by the clustering and dissociating reactions, because the effect due to the former reaction is too small, and the effect due to the latter produces a contrary result to explain the phenomenon. One possible explanation for the phenomenon is that as the energy of the ion increases with *E/N*, the ion comes so close as to experience details of molecular structure. The average energy of Li^+ in N_2 gas at 30 °C and $E/N = 90$ Td is calculated to be 0.17 eV using the equation developed by Wannier.[23]

If Blanc's law is assumed correct, the mixing ratio of the gas is obtained from the mobility in the mixture. Many experimental results support the fact that Blanc's law holds at low *E/N*. Therefore, we may use Blanc's law on the H_2 and N_2 gas mixtures at $E/N = 15$ Td to estimate the mixing ratios. In Fig. 4 the reciprocal mobilities at $E/N = 31$, 93, and 173 Td are plotted as a function of the mole fraction of N_2 gas. For abbreviation, the points for $E/N = 15$ Td are omitted except in pure component gases. These omitted plots are on a straight line passing through the two points corresponding to the pure gases.

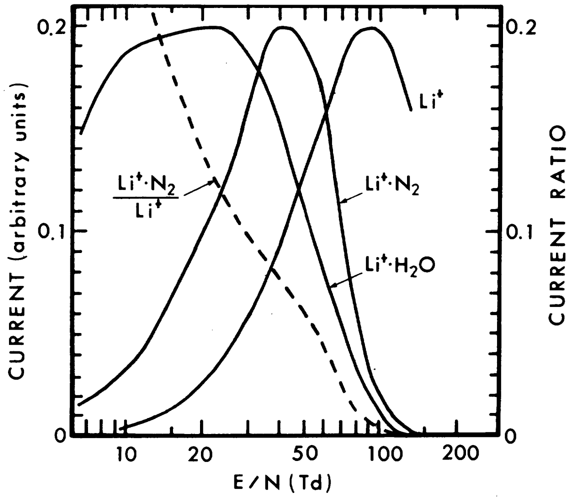

FIG. 5. Current variations with *E/N* for Li^+, $Li^+\cdot N_2$, and $Li^+\cdot H_2O$ on the electron multiplier when the N_2 gas is at 1 Torr and the drift length is 90 mm. Dotted line, the current ratio of $Li^+\cdot N_2$ to Li^+.

Since the temperature changed for each measurement, each plot in Fig. 4 is not the result measured at the same values of *E/N*. The plots for $E/N = 15$ Td lie in the range from 15.5 to 15.9 Td, 31 from 31.0 to 31.8, 93 from 91.9 to 95.1, and 173 from 171 to 176 Td. However, the variations in the reciprocal mobilities within these different ranges of *E/N* are less than 4% even at large values of *E/N*. The values of the reciprocal mobilities for $E/N = 93$ Td obtained at the beginning and the end of the measurement for each mixture are in good agreement. This fact shows the constancy of the mixing ratio of each gas during the measurements. The reciprocal mobilities at $E/N = 31$ and 93 Td seem to change linearly with the mole fraction of N_2 gas. On the other hand, the plots for the reciprocal mobilities at $E/N = 173$ Td show slight deviation from Blanc's law.

IV. DISCUSSION

It is expected that the deviation of mobility from Blanc's law occurs because the collision cross section varies with velocity of the ion relative to that of gas molecules. In both H_2 and N_2 gases, the mobility of Li^+ depends greatly on the ratio *E/N* at large *E/N*. Moreover, inelastic collisions may occur in both gases at large *E/N*. In such a case, the theory of Milloy and Robson does not give a reasonable value for the mobility. In fact, the values calculated from the theory disagree with those obtained for the mixture gas in this experiment at $E/N = 93$ and 173 Td.

It is very complicated and difficult to describe rigorously the motion of the ion in the mixture gas at high values of *E/N* from kinetic theory. In the following, we assume that the drift velocity is related only to the motion of the ions parallel to the electric field and that the motion perpendicular to the electric field affects the arrival time spectrum but not the mean arrival time. If we suppose a cross section of the ion to lose the momentum parallel to the electric field, the mobility of the ion is inversely proportional to the cross section. If only binary collisions of the ion are assumed to play an important role, this cross section for each constituent gas molecule of the mixture is the same as that of each pure gas component at a given drift velocity. Then we obtain from the additivity of the cross section

$$\frac{1}{K_{\mathrm{mix}}(E/N)} = \frac{X_h}{K_h(E_h/N)} + \frac{X_n}{K_n(E_n/N)}\ , \qquad (2)$$

$$K_h(E_h/N)E_h/N = K_{\text{mix}}(E/N)E/N\ , \tag{3}$$

$$K_n(E_n/N)E_n/N = K_{\text{mix}}(E/N)E/N\ , \tag{4}$$

where X_h and X_n are mole fractions of H_2 and N_2, respectively; $K_{\text{mix}}(E/N)$ is the mobility in the mixture at E/N, $K_h(E_h/N)$ in H_2 at E_h/N, and $K_n(E_n/N)$ in N_2 at E_n/N.

The reciprocal mobility in the mixture which satisfies these three equations is obtained using the data in Figs. 2 and 3. The result for $E/N = 173$ Td is shown by the solid line in Fig. 4. It shows that the reciprocal mobility in the mixture is at most 15% smaller than that estimated from Blanc's law. It is seen that the theoretical and experimental results are in good agreement. The calculation with these equations also shows that the reciprocal mobilities are at most 3% larger at $E/N = 31$ Td and 6% smaller at 93 Td than those estimated from Blanc's law. These small deviations could not be observed by the experiment because of the experimental error. However, it will be shown later that the calculating method is also applicable for low values of E/N. It should be noted here that the deviation from Blanc's law at $E/N = 15$ is estimated to be less than 1% by both the calculating methods of Milloy and Robson, and of this work.

The experimental results of Milloy and Robson, which were obtained for E/N less than 100 Td, were also checked by the method of calculation described in this work. The calculation gives a value 1.3 times larger than the deviation from Blanc's law appearing in their results for K^+ ions in the mixture of noble gases. For K^+ ions in the mixture of H_2 and N_2 gases, it gives a deviation one half larger than their experimental results, while their method of calculation gives a deviation three times larger. It is expected that the method of this work would give more accurate values if the mobilities of K^+ were obtained for E/N larger than 100 Td.

The method for calculating mobility used in this work is based on several assumptions. However, in the case of Li^+ in H_2 and N_2 gases, the method enables us to predict the mobility in the mixture with reasonable accuracy over a wide range of E/N from the values of the mobilities in the pure gas components.

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