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# Positive ion mobilities in helium vapor

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The zero-field mobilities of positive helium ions in helium vapor have been measured as functions of both pressure and temperature between 2.0 and 5.2°K. These mobilities are much lower than would be predicted from known ion mobilities at 76°K. These data can be explained in terms of kinetic theory with a clustered-ion hypothesis.

## I. INTRODUCTION

Helium, because of the small interatomic interaction potential, is perhaps the most ideal of the gases. Because of this, transport properties of helium ions in gaseous helium have been extensively investigated in the temperature range from 300 to 76 °K. Recently, much of this work has taken the form of mobility measurements along with mass spectrometric analysis of the particular ionic species involved. These studies have been extended to lower temperatures in order to understand mobility variation with temperature by testing the applicability of the various theories. Patterson[1] has completed one of these intensive temperature-dependence studies. He measured positive-ion mobilities and made a mass analysis of the ions in the temperature range of 300–76 °K, where he observed four different helium ions.

This present investigation was undertaken in order to extend these studies to the temperatures of liquid helium where it was expected that considerable clustering of atoms should occur about the basic stable molecular ions because of the low thermal energy of the background gas. It was felt that the results of this study would help elucidate the phenomenon of nucleation on positive ions. The author was also cognizant of this study's significance to the temperature dependence of ion transport in gaseous helium.

## II. EXPERIMENTAL

In this study the mobilities of positive helium ions in helium vapor have been measured at very low ratios of electric field strength to gas number density. The mobility is defined as the ratio of the average ion drift velocity to the applied electric field strength. These measurements, which used gas temperature $T$, gas pressure $P$, and electric field strength $E$ as the independent variables, were made with time-of-flight techniques using field ionization to produce the ions. The basic method of measurement and the ion source have been successfully used for ion mobility measurements in liquefied gases and have been described elsewhere.[2] Only a brief synopsis is given here to illustrate improvements in technique.

Figure 1 is a diagram of the ion source and measurement cell. $A$ is the etched tungsten wire which is used for the field ionization and ion source. $B$-$C$ is the electronic gate used to control the ions entering the drift space $C$-$E$. The grid electrode $D$ was placed in the center of the drift space $C$-$E$ primarily to decrease the induced pickup from the ion source and ion gate by the sensitive amplifier connected to the collector electrode $E$. It also served to hold the electric field more uniform in the ion drift space. All electrodes were machined from nickel and the grids were nickel-plated fine mesh with square holes 0.001 in. on a side. Each grid had approximately 25% open area.

In practice, the collector $E$ was essentially at ground potential. Electrodes $C$ and $D$ were at po-

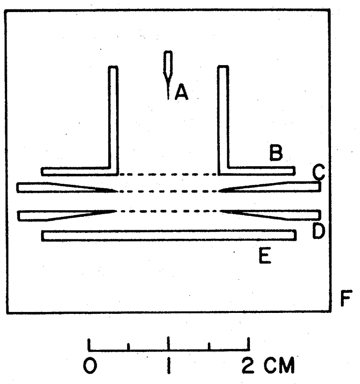

FIG. 1. Diagram of the electrode assembly used to measure the helium-ion mobility. $A$ is the ion source, region $B$-$C$ is the ion gate, region $C$-$E$ is the drift space, $E$ is the collector electrode, and $F$ is the copper can which serves as an electric shield and cell for the vapor.

tentials above ground of $V$ and $\frac{1}{2}V$, respectively, and a square-wave potential was applied to electrode $B$ whose average potential was $V$. The square wave produced the electric fields in the space $B$-$C$ to operate the ion gate.

The procedure used was to open gate $B$-$C$ to allow ions to enter the drift space. This gate was left open until the current collected by the collector electrode $E$ was constant and then the gate was closed until the ions were swept out of the drift space $C$-$E$. The time of flight of the ions from $C$ to $E$ is the time for the ion swarm to be swept from the drift space. Ideally, after the gate $B$-$C$ is closed the current collected by the collector $E$ remains constant until all of the ions are swept from the region $C$-$D$ of the drift space and then the collected current decays linearly until all ions are swept from drift space region $D$-$E$.

The collector current was amplified with a PAR Model 113 broadband dc amplifier before being signal averaged with a PAR Model TDH9 waveform Eductor. The entire measurement cell was placed in a sealed copper can and then immersed in a liquid helium bath. The copper can was evacuated and then filled with purified helium vapor. The pressure of this vapor was measured with a mercury manometer using a cathetometer that measured to an accuracy of ±0.1 mm. The temperature of the helium bath was maintained by controlling the vapor pressure of the helium bath with a sensitive pressure regulator. The temperature of the copper can was monitored electronically with a germanium resistor using a sensitive Wheatstone-bridge circuit.

During the course of this experiment the electric field strength was kept low enough so that the measured mobility was essentially the zero-field mobility. The actual electric fields used were varied from as low as 10 V cm$^{-1}$ to, in some cases, as high as 1000 V cm$^{-1}$. The larger fields were used only when the gas density and temperature were sufficiently high to retain the low-field approximation. Thus, in all of the measurements, the ratio $E/N$ of the electric field strength to the gas density was kept low so that low-field conditions prevailed. For most of these measurements the ratio $E/N \lesssim 10^{-19}$ V cm$^2$ which is about two orders of magnitude smaller than the low-field criterion commonly quoted.[3] Care was taken to ensure that the field energy was negligible compared with the thermal energy by keeping the electric field low enough so that the condition[3]

$$(M/m + m/M)eE\lambda \ll kT$$

was satisfied even where ion clusters of 100 or more atoms might occur. $M$ and $m$ are the atomic and ionic masses, respectively, and $eE\lambda$ is the energy gained in a mean free path $\lambda$ from the field $E$ for an ion of charge $e$. Charge densities were kept low so that there was negligible field distortion due to space charge in the drift space.

The uncertainties in the mobility data are at most ±3%. Most of this statistical error comes from uncertainty in measuring the times of flight of the ions. The drift space has been verified to within ±0.5% at liquid-nitrogen temperatures. Any uncertainty in drift-space determination would yield a constant error.

As many as 20 to 30 individual time-of-flight traces were measured at various electric field strengths for a given pressure and temperature. Each of the mobilities reported in this article was the result of a linear regression of ion drift velocity on electric field using time-of-flight data. Typical correlation coefficients for these regressions were better than 0.999.

The uncertainties in the vapor pressure measurements are on the order of ±0.5% at 2.0 °K to on the order of ±0.05% at 5.0 °K. It was determined that the temperature was constant and known to within $\pm 2 \times 10^{-3}$ °K or better in every case.

## III. DISCUSSION OF RESULTS

It has been found that the zero-field mobilities of the positive ions in this study are explainable in terms of the Chapman-Enskog[3] kinetic theory which determines a mobility equation

$$K = \frac{3}{16}\left(\frac{1}{m}+\frac{1}{M}\right)^{1/2} \frac{(2\pi)^{1/2}}{(kT)^{1/2}} \frac{e}{N} \frac{1}{\overline{\Omega}^{(1,1)}}, \qquad (1)$$

where $K$ is the zero-field mobility and $\overline{\Omega}^{(1,1)}$ is an averaged diffusion cross section with units of area. The other symbols are as previously noted. In the case of a hard-sphere-type interaction the cross section is expressed as $\pi d^2$, where $d$ is the sum of the atomic and ionic radii.

The ion mobility was not viscous limited in the range of this experiment except perhaps in the vicinity of the critical point where $T > 5.1$ °K. Transport of ions through a gas should only be viscous limited if the ion size is greater than the interatomic mean free path. Springett[4] has determined that this should be true in helium only if the gas density exceeds 0.02 g cm$^{-3}$.

Figure 2 shows the ion-mobility data presented as a function of gas pressure at various constant temperatures. It is determined that the uncertainties in these data are less than or on the order of the size of the circles used to plot the data points. Thus no error bars have been included in Fig. 2. All of the data points for a given temperature have been connected by solid curves to help guide the eye. It is noted that these curves are approximate-

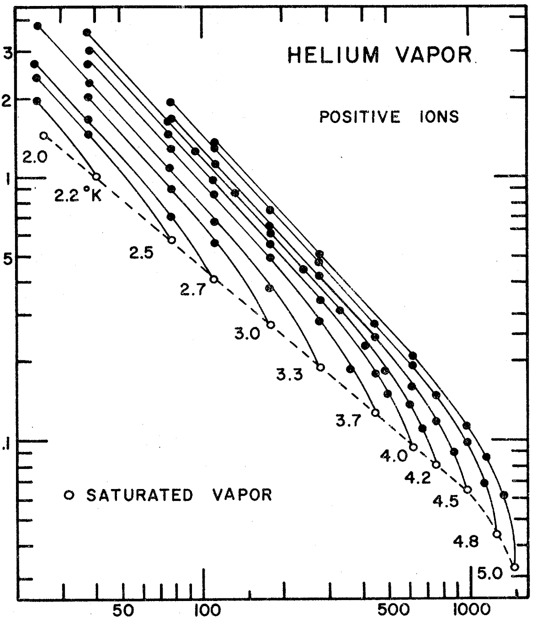

FIG. 2. Helium-ion mobility in its vapor presented as a function of pressure at various constant temperatures. The curves connecting the data points have been drawn to aid in following the constant temperature data.

ly linear for pressures which are less than about 50% of the pressure corresponding to saturation of the vapor. The measurements made in saturated vapor for each temperature are presented as open circles and are connected with the dashed curve. This curve is also linear in the range $2 \leqslant T \leqslant 4.5$ °K. In these linear regions the mobility has been found to vary approximately as $N^{-1}$ as predicted by Eq. (1). This indicates that the diffusion cross section can at most have a weak dependence on $N$ in these regions of rarefied pressure. In the curved sections the mobility decreases at a much faster rate with $N$ than predicted by a $N^{-1}$ dependence. This can be explained because of two effects. First, it is quite plausible that a cluster of atoms is formed about the ion and that the size of the cluster at these higher pressures is dependent on the gas density as well as on the gas temperature. Second, at the higher densities tertiary and higher orders of collisions may become significant. Equation (1) is derived for binary collisions only.

Experimental evidence for clustering comes from several sources. Patterson[1] showed that the chemically stable ion at low $E/N$ at 76 °K was the molecular ion $He_3^+$. Helms[5] has recently made an intensive study of helium-ion mobilities in helium gas at 77 °K as functions of $E/N$. While Helms verified the results of Patterson he also observed the ions $He_2^+$ and $He_4^+$ at 77 °K. Others[6] have found $He_4^+$ in helium plasmas. Dahm and Sanders[7] have observed effective masses of positive helium ions on the order of 75 helium atomic masses in saturated helium vapor at 4.2 °K. They used a microwave technique for this determination.

It has been customary among investigators working in the field of gaseous electronics to remove the usual $N^{-1}$ dependence of mobility data by normalizing the data to a standard gas density of $N_0 = 2.69 \times 10^{19}$ molecules/cm³. This is accomplished by the equation $K_0 = KN/N_0$. The reduced mobility $K_0$ can then be more easily compared with other data at various temperatures because the temperature dependence of $K_0$ is usually weaker.

Figure 3 shows the reduced mobility data of the present study compared with data of others[1,8–11] taken at higher temperatures. The ion $He_2^{+*}$ as noted on the graph is believed to be the diatomic ion in an excited vibrational state $[He_2^+(^4\Sigma_2)]$.[1,12] It is observed that my data at liquid-helium temperatures follow the trend of the other data for the molecular-ion mobility to decrease with temperature. However, my data for the reduced mobility are considerably lower than would be expected from the theory of an unclustered ion. For example, the Langevin-theory[13] mobilities for $He_2^+$ and $He_3^+$ in the 0 °K limit are much higher than those actually observed except for those data near the helium critical point. Here again this can be explained in terms of an ion cluster model. Extensive clustering at the low temperatures will increase the diffusion cross section causing a lower than normal mobility. If the cluster is large enough one expects the surface tension of liquid

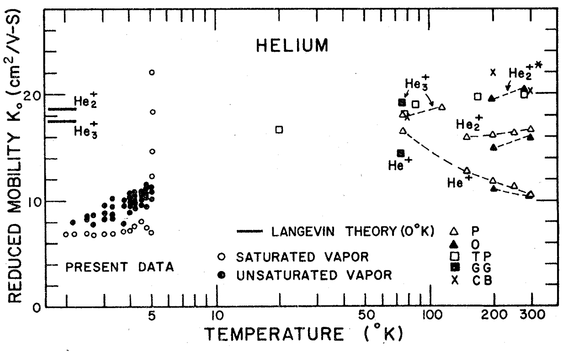

FIG. 3. Reduced zero-field mobility of positive helium ions vs temperature. Comparison of these data is made with data of Patterson (P), Orient (O), Tyndall and Pearce (TP), Gerber and Gusinow (GG), and Chanin and Biondi (CB) at higher temperatures. The predictions of the Langevin theory in the 0 °K limit are also indicated for two molecular ions.

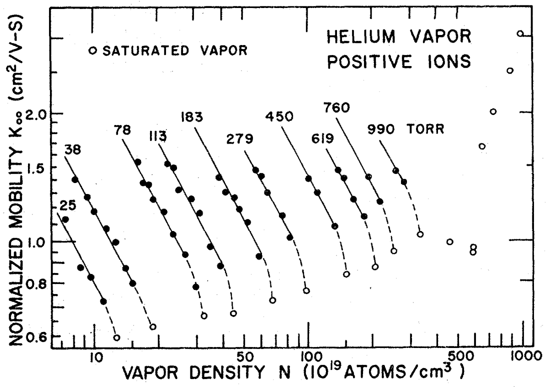

FIG. 4. Positive helium-ion mobility which has been normalized for both gas density and temperature vs gas density presented at various constant gas pressures. The normalized mobility $K_{00}$ will vary inversely with the average diffusion cross section $\overline{\Omega}^{(1,1)}$.

helium to play a significant role in holding the cluster together.[14] As the critical point is approached the surface tension approaches zero thus allowing the cluster to break up. Only the induced dipole-ion interaction would hold the cluster together near the critical point. The density fluctuations that are known to occur near the critical point would probably enhance cluster breakup also.

Equation (1) contains a $T^{-1/2}$ factor for the temperature dependence. Virtually all mobility theories contain this factor including the viscous limited case for an ideal gas. In order to better observe the dependence of $\overline{\Omega}^{(1,1)}$ on the temperature and density the reduced-mobility data have been normalized for temperature using the $T^{-1/2}$ term and portrayed in Fig. 4. This normalized mobility $K_{00}$ can be expressed in terms of the mobility or the reduced mobility as

$$K_{00} = K(N/N_0)(T/T_0)^{1/2} = K_0(T/T_0)^{1/2} ;$$

where $T_0 = 273.16$ °K has been chosen as the standard temperature for normalization. It should be pointed out that the values of the reduced mobility $K_0$ and the normalized mobility $K_{00}$ are somewhat more uncertain than the raw mobility measurements because of increased error due to uncertainties in vapor density. However, it is determined that the largest variation in the data points of Fig. 4 due to combined error would still place the points within a circle no more than 50% larger in radius than the solid circles themselves. The two-dimensional error bars have been intentionally omitted to avoid complicating the figures.

Empirically these data for the normalized mobility $K_{00}$ form a relatively simple functional relationship at low densities when represented as a function of density at constant pressure. Under the condition of densities somewhat lower than the saturation value for a given pressure the data fall on straight lines within experimental error and it has been found that to a very good approximation these data can be represented by the empirical equation $K_{00} = (\alpha P - \beta)/N$. If $P$ is in atm and $N$ is in units of $10^{19}$ atom/cm³, the constants $\alpha$ and $\beta$ take on values of 226 and 0, respectively, for $P \lesssim 405$ Torr and values of 319 and 49, respectively, for $990 \gtrsim P \gtrsim 405$ Torr. This empirical equation yields values of $K_{00}$ which are generally consistent with the experimental values to within ±5% and the discrepancy is never greater than about ±10%. The parameters $\alpha$ and $\beta$ were determined by a least-squares analysis of the normalized mobility $K_{00}$ with respect to vapor density and pressure. Correlation coefficients of 0.999 or better were obtained in this analysis. Since the pressure, density and temperature are related by the equation of state of helium the virial equation can be used to express this empirical relation for $K_{00}$ in terms of temperature and density. The result is

$$K_{00} \cong \alpha kT(1 + B_2(T)N + B_3(T)N^2 + \cdots) - \beta/N ,$$

where the virial coefficients $B_2$, $B_3$, ... are small compared to 1. It is seen from this equation that $K_{00}$ has only a weak dependence on density for $P \lesssim 405$ Torr. It is suggested that the rather abrupt change in the constants $\alpha$ and $\beta$ near $P \cong 405$ Torr is caused by a basic change in the ion complex or else tertiary collisions become important for $P \gtrsim 405$ Torr.

## IV. CONCLUSIONS

In concluding, it seems apparent from these mobility data that considerable clustering of atoms about the positive ions takes place in helium vapor. It appears that the basic ion transport phenomena in helium vapor can be explained with kinetic theory if clustered ions are postulated. On the other hand, a detailed understanding of the ion clustering or nucleation process is yet to come. It is hoped that the results of this study will inspire theorists working in this general area to investigate these phenomena in helium vapor. More-detailed mobility measurements are currently being obtained in this laboratory in the regions of higher densities near saturated vapor conditions. Particular emphasis is being given to measurements in the vicinity of the critical point temperature.

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