Mobilities of Cesium Ions in Cesium*

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Measurements have been made of the mobilities of cesium ions using a pulsed-discharge technique. In the present studies two ionic species were observed; however, over the entire E/p_0 and p_0 range investigated the "fast" ion type was dominant. The present values are compared with the available theoretical values and also previous experimental results. From the comparison we tentatively identify the dominant ion as being Cs_2^+; the less frequently observed ion is believed to be Cs^+. The normalized mobility values corresponding to a gas density of 2.69×10^{19} atoms/cc for Cs^+ and Cs_2^+ are 0.075 and 0.21 cm²/V sec, respectively, over the temperature range of approximately 579–679°K.

I. INTRODUCTION

In recent years considerable interest has been shown in alkali vapors. In particular numerous experimental and theoretical studies have been performed on the properties of cesium vapor. At the present time the only published experimental measurements of the mobilities of positive ions in cesium are those reported by Dandurand and Holt[1] and Chen and Raether[2] using microwave techniques. The thermal mobility value obtained by Dandurand and Holt was 0.065 cm²/V sec, believed to correspond to that of Cs_2^+; by contrast Chen and Raether using cesium and cesium-helium mixtures obtained a value of 0.4 cm²/V sec believed to correspond to the case of Cs^+ in cesium. The present study was initiated in an attempt to obtain reliable measurements of the mobilities of positive cesium ions moving in their parent gas, using direct time-of-flight techniques. The following article describes the results of this investigation and presents tentative arguments concerning the ion identities.

II. APPARATUS

The present method is similar to that used previously[3] to study ionic mobilities in a number of different gases. The method consists of generating a pulsed discharge between the discharge electrode of the experimental tube and a grid held at ground potential. Some of the ions created in this manner pass through the grid into the drift region where their motion under the influence of a constant applied electric field induces a current in the external circuit. From an analysis of the induced current the ion transit times can be determined. The experimental tube used in the present studies is shown schematically in Fig. 1. The tube, which was constructed from No. 304 stainless steel, uses ceramic insulators to minimize the leakage-resistance problem. In addition the tube used four gold wire gaskets to facilitate cleaning and assembly operations. All portions of the plumbing connected to the tube consisted of cesium-compatible materials; in particular stainless steel and nickel were used. The discharge and drift distances could be controlled externally to the ovens containing the tube by means of micrometer-driven bellows assemblies. The discharge and drift distances could be varied out to 2.5 and 5.0 cm, respectively, with an accuracy of 10^{-3} cm, thus permitting one to optimize the discharge characteristics and, also, to obtain differential measurements free of injection errors. Such errors may arise since the ions injected through the grid from the discharge region have energies greater than that typical of their equilibrium drift motion. Thus, the initial portion of their transit is not characteristic of their equilibrium motion. Not shown in Fig. 1 are electrical shields used to isolate the discharge and drift regions of the tube.

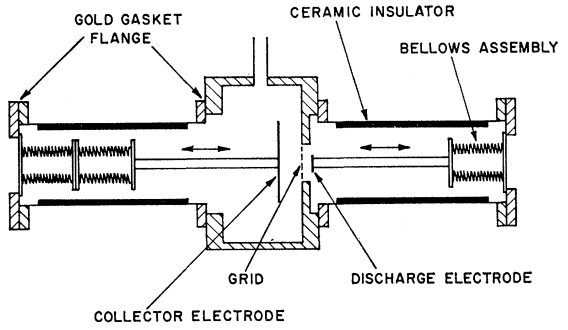

FIG. 1. Schematic drawing of the experimental tube.

Figure 2 shows a schematic drawing of the experimental tube and a portion of the high vacuum station[4] on which it was mounted. The cesium used in the present measurements (99.9% pure) was contained in evacuated pyrex ampules in a copper finger whose temperature could be controlled independently of the rest of the system. Following extended bakeout of the experimental tube at temperatures in excess of the operating temperature of the system, the cesium ampules were opened by pinching the copper tubing. The cesium could then be introduced into the system by raising the temperature of the copper finger to achieve the desired cesium pressure. In the initial studies cumulative degassing of the experimental tube

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[1] P. Dandurand and R. B. Holt, Phys. Rev. **82**, 278 (1951).
[2] C. L. Chen and M. Raether, Phys. Rev. **128**, 2679 (1962).
[3] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).
[4] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

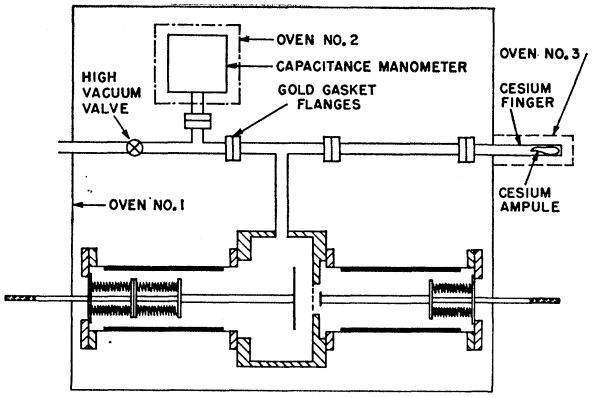

FIG. 2. Schematic drawing of the experimental tube and a portion of the high-vacuum gas handling system. The broken and solid lines refer to ovens surrounding various parts of the apparatus.

while the measurements were being conducted, in spite of previous extended high-temperature bakeout, was found to be a serious problem. Thus, reliance on a knowledge of the temperature distribution throughout the system obtained from an extensive thermocouple system, to infer the pressures inside the tube, gave erroneous results if the system had been maintained at high temperatures for extensive periods of time.

In order to have an independent check of the cesium pressures, the capacitance manometer was incorporated into the system to measure the pressures directly. In order that the manometer could be used reliably a special oven was made to maintain the manometer temperature constant with less than 1°C variation. In practice the measurements were made by first baking the entire system for at least 15 h at temperatures in excess of the operating temperature at which the measurements were to be made. At room temperature the system achieved pressures $\sim 10^{-9}$ Torr following bakeout. The system was then raised to the desired operating temperature for approximately 15 h; the high-vacuum valve which could be opened and closed externally to the ovens was then closed, and the cesium finger raised to the desired temperature (the temperature of the cesium finger was always the lowest temperature in the system). In order to maintain the leakage resistance of the insulators at sufficiently high values, $\sim 10^5$ Ω, localized heating of the ceramic insulators was controlled by means of heating tapes not shown in Fig. 2.

III. RESULTS

The measured values of the drift velocity, w_i, versus the electric field to pressure ratio, are shown in Fig. 3. The pressure p_0 is the normalized pressure, i.e., $p_0 = 273\, p/T$, where T is the gas temperature. The gas temperatures refer to the temperature of the cesium in the experimental tube where the measurements are performed and were determined from an extensive thermocouple system. For comparison of the present data with the drift velocity versus E/p_0 behavior predicted by Wannier,[5] lines of slope unity at low E/p_0, and one-half at high E/p_0 are shown in Fig. 3. The slope of one-half for the high-field case is typical of ionic motion where the dominant ion-atom interaction is either a short-range repulsion or the resonance interaction of charge transfer. For the high-field case, the polarization interaction which has a cross section varying inversely with the velocity of approach of the particles, and, thus, is not significant in this range, would lead to a velocity varying directly with E/p_0. In the low-field region all three ion-atom interactions lead to a drift velocity varying directly with E/p_0. From Fig. 3 it will be noted that the variation of the drift velocity with E/p_0 for the case of the "slow" ion has an anomalous behavior in the vicinity of $E/p_0 = 60$–100. At the present time the reason for this behavior is not understood; however, similar variations have been observed previously[6] in other gases and have been attributed to changing ion identity.

Figure 4 shows a plot of the corresponding normalized mobility values. The mobility μ_0 refers to a gas density of 2.69×10^{19} atoms/cc (equivalent to 760 Torr at 0°C). It will be noted from Fig. 4 that there does not appear to be a consistent variation of the data with temperature over the range investigated (579–679°K). The zero-field mobility values for the ions observed in the present studies as determined from Fig. 4 are 0.21 ± 0.01 and 0.075 ± 0.01 cm²/V sec over the temperature range from 579–679°K. For comparison with the present values, Fig. 4 shows the mobility values measured by Dandurand and Holt[1] and also by Chen and Raether.[2]

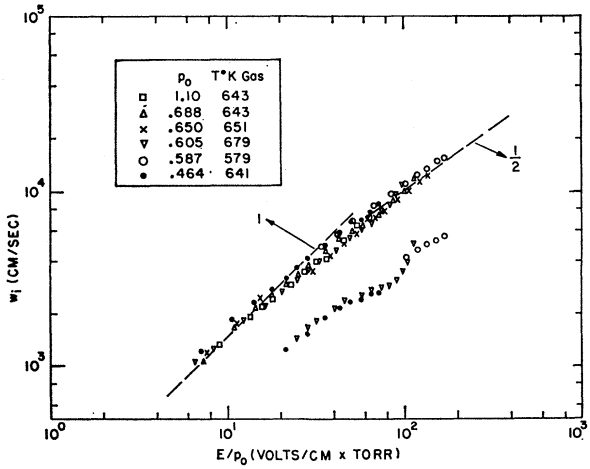

FIG. 3. The variation of the drift velocity with E/p_0. The lines of slope unity and one-half are in accordance with the variation predicted by Wannier.

[5] G. H. Wannier, Phys. Rev. **83**, 281 (1951).
[6] R. N. Varney, Phys. Rev. **89**, 708 (1953).

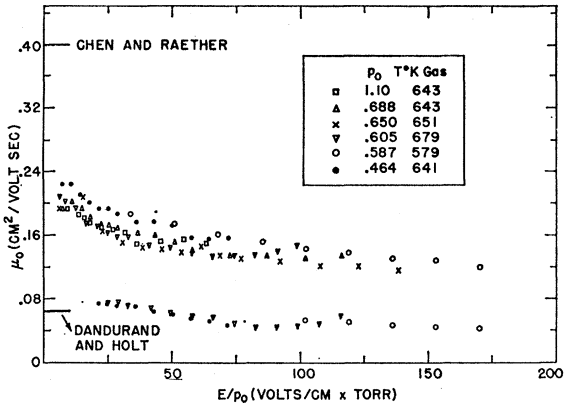

FIG. 4. The variation of the normalized mobility with E/p_0. The values on the ordinates refer to those obtained previously using microwave techniques.

The mobility value reported by Chen and Raether was obtained over the temperature range from 450–550°K; the gas temperature in the mobility measurements of Dandurand and Holt was not specified. It will be noted that the present low-mobility ion is in fair agreement with the value reported by Dandurand and Holt. The value reported by Chen and Raether, however, lies considerably above the present results. More recent studies and re-examination of their earlier data by Chen[7] indicates a cesium ion mobility value of approximately 0.2 cm^2/V sec over a range of temperatures from 464–478°K in contrast to their earlier value of 0.4 cm^2/V sec. In addition these studies indicate an apparent increase of the mobility value up to 0.28 cm^2/V sec corresponding to a temperature of 500°K. The new value at low temperatures reported by Chen is in good agreement with that obtained in the present studies for the "fast" ion. Extrapolations of their results to the temperatures at which the present measurements were made would give values in excess of those measured in the present study. This apparent discrepancy could, however, be resolved if the mobility passes through a maximum in going from the temperatures at which their measurements were made, to the temperatures at which the present measurements were conducted. From Figs. 3 and 4 it will be noted that the low-mobility ion was observed only at moderate E/p_0 values and at low pressures. In all the measurements over the entire range of pressures and E/p_0 values investigated, the dominant ion was that with the higher mobility value.

IV. DISCUSSION

It is of considerable interest to speculate as to the identities of the ions observed under the present experimental conditions. This may be done by comparison of the experimental results with values calculated using the available theories of ionic mobilities.

[7] C. L. Chen (private communication).

For the case of Cs_2^+ moving in cesium, no satisfactory theory exists at the present time, in view of the diatomic nature of the ion. Thus one must resort to the "classical" mobility treatments such as that given by Langevin.[8] Recognizing the limitations of the Langevin theory, some confidence, however, may be obtained when using the polarization limit ($T=0$°K) of the theory for the case of Cs_2^+ in cesium in view of the strongly polarizable[9] nature of the gas. Thus, for example, it can be shown that the percent error involved in using the polarization limit for noble-gas diatomic ions moving in their parent gas, as well as various monatomic alkali ions moving in the noble gases, decreases strongly with increasing polarizability of the gas. Extrapolations of such estimates to the case of cesium lead one to expect that in spite of the oversimplification of the ionic "model," the theoretical value should be within less than 10% of the experimental result. Comparison of the mobility value of the "fast" ion 0.21 with the Langevin value 0.20 strongly suggests that this ion is Cs_2^+.

Since at the temperatures of interest in the present experiment, cesium is predominantly in atomic form,[10] the dominant ion-atom interaction for the case of Cs^+ moving in cesium, will be charge transfer. At the present time experimental values of the charge-transfer cross section are not available at the low energies of interest in mobility measurements. Thus, in order to calculate the mobility, the high-ion-energy data must be extrapolated[11] down to low energies. This extrapolation involves several difficulties, arising from discrepancies between the high-energy values[12–15] as well as the magnitude of the energy range over which the extrapolation must be performed. Sheldon[16] using an approximate form of the charge-exchange cross section has extrapolated the data given in Refs. 12–15 and subsequently calculated the corresponding mobilities. This extrapolation was performed assuming a variation of the cross section Q with relative ion-atom energy E of the form

$$Q=(A-B\ln E)^2, \tag{1}$$

where A and B are constants.

[8] P. Langevin, Ann. Chim. et Phys. **5**, 245 (1905).

[9] Recent experimental measurements of the polarizability of cesium yield values ranging from 42–52.5×10^{-24} cm^3. See G. E. Chamberlain and J. C. Zorn, Phys. Rev. **129**, 677 (1963). The value of 52.5×10^{-24} cm^3 used in the Langevin estimate for the mobility of Cs_2^+ in cesium was that obtained by A. Salop, E. Pollack, and B. Bederson, Phys. Rev. **124**, 1431 (1961).

[10] J. K. Theobald (private communication). Using the Gibson-Heitler equation, Theobald has estimated two percent in the molecular state for saturated cesium vapor at 550°K.

[11] L. M. Chanin, Bull. Am. Phys. Soc. **7**, 635 (1962).

[12] R. M. Kushnir, B. M. Palyukh, and L. A. Sena, Bull. Acad. Sci. USSR Phys. Ser. English Transl. **23**, 995 (1959).

[13] A. M. Bukhteev and Yu. F. Bydin, Bull. Acad. Sci. USSR Phys. Ser. English Transl. **24**, 966 (1960).

[14] R. M. Kushnir and I. M. Buchma, Bull. Acad. Sci. USSR Phys. Ser. English Transl. **23**, 989 (1959).

[15] R. C. Speiser, Electro-Optical Systems, Inc., Pasadena, California, E.O.S. Report 1583, 1961 (unpublished).

[16] J. W. Sheldon, J. Appl. Phys. **34**, 444 (1963).

TABLE I. Comparison of experimental and theoretical mobilities in cesium.

Experimental μ_0 (cm^2/V sec)			Theoretical μ_0 (cm^2/V sec)	
Present (579–679°K)	Dandurand and Holt Cs_2^+	Chen and Raether Cs^+ (450–550°K)	Langevin polarization limit Cs_2^+ ($T=0$ limit)	Charge exchange calculation Cs^+ ($T=300$°K)
0.21				0.074[a]
				0.036[b]
———	0.065	0.4	0.203	0.088[c]
0.075				0.055[d]

[a] Ref. 12. [b] Ref. 13. [c] Ref. 14. [d] Ref. 15.

Table I shows a comparison of the various experimental and theoretical estimates. From such a comparison we conclude that the "slow" ion observed in the present studies is probably Cs^+.

It was noted in Sec. III that the "slow" ion we believe to be Cs^+ was observed only under certain conditions, in particular at low pressures and at moderate E/p_0 values. Moreover, the "fast" ion we identify as Cs_2^+ was the dominant ion over every pressure and E/p_0 range investigated. The failure to observe Cs^+ at high pressures may be understood if the conversion frequency to Cs_2^+ is moderately high. On the other hand, the failure to observe Cs^+ at low pressures at low E/p_0 may be simply a matter of resolution, in view of the fact that the amplitude of Cs_2^+ was at least a factor of ten times greater than that of Cs^+. It should also be noted that the dominance of Cs_2^+ over Cs^+ may imply that the cross section for the associative ionization reaction involving excited states[17] of the cesium atom to form Cs_2^+ is very great.

The interpretation of the present results cannot be easily reconciled with the interpretations of the previous microwave measurements. In particular the ion which Dandurand and Holt believed to be Cs_2^+ had a mobility value more consistent with that corresponding to Cs^+. In the early measurements of Chen and Raether the value of 0.4 cm^2/V sec was attributed to Cs^+. Their revised value of approximately 0.2 cm^2/V sec for temperatures from 464–478°K is in agreement with that obtained in the present work for temperatures from 579–679°K. Comparison of this value, however, with the available theoretical estimates suggests that the ion is probably not Cs^+ but rather Cs_2^+. Finally, for the general case of an atomic ion moving in its parent gas, the mobility value will decrease with increasing temperatures.

[17] F. L. Mohler and C. Boeckner, J. Res. Natl. Bur. Std. **5**(RP186), 51 (1930). Their estimated values for the distance σ between atom centers at collision, for the case of interactions of excited atoms in the $5P$ state with normal atoms lie between 10^{-7} and 3×10^{-7} cm.

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