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Mobilities of Cesium and Rubidium Ions in Their Parent Vapors

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The mobilities of Rb^+ and Rb_2^+ in rubidium vapor, and of Cs^+ and Cs_2^+ in cesium vapor have been measured. The mobilities of the molecular ions agree well with values calculated from the Langevin theory in its polarization limit. The mobilities of the atomic ions are consistent with the predictions of simple resonant charge transfer theory. Rate constants for the reactions of the atomic ions with diatomic molecules to give diatomic molecular ions have been obtained.

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*Alfred P. Sloan Fellow.

In a previous paper[1] we described experiments in which the diatomic molecular ions of cesium, rubidium, and potassium were produced by photoexcitation of the gaseous atoms followed by a Horbeck-Molnar ionization process:

$$\mathrm{Cs} + h\nu \longrightarrow \mathrm{Cs}^{*}\ (\mathrm{mP}),$$
$$\mathrm{Cs}^{*} + \mathrm{Cs} \longrightarrow \mathrm{Cs}_2^{+} + e.$$

We noted there that the mobilities of both the atomic and molecular gaseous ions of the alkalis could be obtained from measurements of the phase shift between the chopped exciting light and the current at the ion collector, and we gave preliminary values for the mobilities of Rb^+ and Rb_2^+ in their parent vapor. We also remarked that space charge effects caused by copious thermal electron emission from the ion collector electrode could lead to inaccuracy of the measured mobilities. In the present paper we report ion mobility measurements for the rubidium and cesium systems that have been performed with a refined apparatus designed to eliminate space charge effects.

Experimental

The materials, optical system, and electronics have been described previously. The photoionization cell was constructed of quartz with plane parallel platinum electrodes. As shown in Fig. 1, a 5.0x9.0 cm screen grid of 200 mesh, 0.5 mil tungsten wire was located 0.3 cm in front of the collector electrode. The collector itself was 2.0x5.5 cm, and was surrounded by a guard ring of 5.0x9.0 cm outside dimensions. The repeller electrode, separated from the collector by 3.8 cm, was the same size as the screen. The screen was maintained at 0.10 the potential of the repeller, and formed an equipotential surface that divided the cell into the large ion migration region between the repeller and screen, and the small detection region between the screen and collector. There is an electron current, which may be space charge limited to some extent, between the collector and grid, but this current is unaffected by the presence of ions in the migration region. An ion that passes from the migration region through the screen into the detection region causes space charge neutralization and is registered as an enhancement of the thermal electron current from the collector. Thus the detecting region is also the first stage of amplification of the ion current.

The light beam, which was 0.15x1.0 cm in cross section, passed through the cell parallel to the electrodes. It could be located at any one of five equally spaced positions in the migration region, and thus the distance the ions had to travel to the detector region could be varied in equal increments from 3.0 to 0.46 cm. By this technique, any uncertainties due to the finite thickness of the detecting region could be eliminated, and it could be ascertained that the field in the migration region was not distorted by space charge or other effects for field strengths greater than 3V/cm.

Molecular ions were produced by exciting rubidium and cesium atoms to the 8P and 9P states respectively. It is believed[1] that the ions produced consequent to these excitations are exclusively molecular. Atomic ions were produced by radiation in the photoionization continuum region.

The exciting light was chopped at several frequencies ranging from 578 to 1500 $\sec^{-1}$. As long as the migration time of the ions was shorter than the chopping period, the results were independent of the frequency used. Migration times long compared to the chopping period resulted in distorted wave forms and consequently chopping frequencies were selected so that the measured phase shift of the ion current was less than 100°.

The pressures of the alkali metal vapors were set by the thermostatically controlled (±0.1°C) temperature of the appendix tube that contained the liquid metal. The temperature was measured with an iron-constantan thermocouple, and the vapor pressure data of Kvater and Meister,[2] Taylor and Langmuir,[3] and Goldberg[4] were used to calculate the pressure. The two determinations[2,3] of the vapor pressure of cesium are in excellent agreement in the temperature range used in our work. In addition, the boiling points of cesium and rubidium calculated from the vapor pressure equations of Kvater and Meister and Goldberg agree well with the measured boiling temperatures. These vapor pressure data appear to be quite reliable.

Results and Discussion

The measured values of the drift velocity, w_i, are plotted as a function of the electric field to pressure ratio for rubidium and cesium in Figs. 2 and 3. The pressure P_o is the normalized pressure, i.e., $P_o = 273\ P/T$, where T is the temperature of the alkali metal vapor. Lines of slope unity and one-half are drawn to indicate the limiting behavior expected at low and high values of E/P_o, respectively. The low E/P_o case corresponds to the ion drift velocity being much smaller than the random thermal velocity. The root-mean-square velocities for rubidium and cesium atoms in the temperature range involved are 4.3×10^4 and 3.5×10^4 cm/sec respectively, and thus our data lie near the transition between the high and low E/P_o regions.

For the diatomic ions particularly, the data show that w depends very nearly on E/P_o to the first power. A dependence of w on E/P_o to the first power even at high values of E/P_o is expected if the predominant term in the ion-neutral potential is due to the ion-induced dipole interaction that varies at $1/r^4$. Our data suggest that the mobilities of the diatomic ions in their own vapor may be described to a first approximation by the classical Langevin theory in its polarization limit.

The drift velocity of Rb^+ varies as E/P_o raised to a power very slightly less than unity under our conditions, as Fig. 2 shows. The data for Cs^+ are considerably more extensive, and in Fig. 3 the departure from the slope of unity is clear.

Figures 4 and 5 show the normalized mobility μ_o plotted as a function of E/P_o. The mobility μ_o refers to a gas density of 2.69×10^{19} atoms/cc. To deduce the true zero field mobility, it is desirable to make measurements at as low a value of E/P_o.

as possible. However, this involves considerable experimental difficulty, for at small values of the electric field the signal strength decreased, and at the higher pressures the windows of the cell darkened rapidly. The estimates of the zero field mobilities based on extrapolation of the best straight lines through all the points are given in Table I. While more extensive data at lower E/P_0 might show some other method of extrapolation to be preferable, it is unlikely that this will lead to any substantial change in the mobility values.

The mobilities of Cs^+ and Cs_2^+ in cesium vapor have been measured previously by Chanin and Steen.[5] Their value of 0.21 cm^2/V sec for the normalized zero field mobility of the ion they took to be Cs_2^+ is in good agreement with our determination for the ion produced by photosensitized ionization. Both determinations agree with the value of 0.20 calculated from the simple Langevin theory for Cs_2^+ in Cs if 52.5×10^{-24} cc is used for the polarizability[6] of the cesium atom. The identity and mobility of this ion seem secure.

Our value of 0.12 cm^2/V sec for Cs^+ is larger than those reported by Chanin and Steen (0.075) and Dandurand and Holt[7] (0.065). It is difficult to find an unassailable reason for this disagreement, except that Chanin and Steen report difficulty in observing this ion, and in fact performed their experiments in a pressure range where we find atomic ions are rather rapidly converted to molecular ions. We did not find the "anomalous" dependence of the drift velocity on E/P_0 observed by Chanin and Steen.

The experimental zero field mobility for Rb_2^+ agrees well with the value (0.283) calculated using the Langevin theory and a polarizability[6] of 40×10^{-24} cc for the rubidium atom. The measured mobility of the atomic ion is approximately 0.6 that of the molecular ion as was true in the cesium system. Mobility ratios in the range 0.6 to 0.8 for atomic and diatomic ions in their parent vapor have been found in the mercury[8] and noble gas[9] systems.

The absolute values of the mobilities of the rubidium ions agree within experimental error with the determination reported previously.[1] In our earlier work, however, the flight time of the molecular ions appeared too short probably because of a combination of molecular ion-electron recombination and space charge effects. Neutralization of the space charge limited electron current by positive ions produces a response at the collector with zero phase shift and ion-electron recombination attenuates the part of the signal that should arrive at the collector with the proper phase shift. This effect can be expected for the alkali metal systems in other mobility apparatuses which employ unshielded collectors. We feel the grid employed in our present apparatus eliminated this difficulty.

Since the atomic ions have a smaller mobility in their parent vapor than the corresponding molecular ions, resonant charge transfer must constitute the dominant contribution to the mobility cross section for the atomic ions. It is of interest to compare our measured mobility cross sections for the atomic ions with predictions of the simple theory of resonant charge transfer. The average mobility cross section is given in terms of the mobility by[10]

$$Q = \frac{2.97\text{x}10^4}{\mu_o \sqrt{mT}}$$

where μ_o is the reduced zero field mobility, m is the atomic mass in amu, and T is the temperature. Our data give Q = $6.3\text{x}10^{-14}$ cm^2 for Rb$^+$ and $7.5\text{x}10^{-14}$ cm^2 for Cs$^+$. Rapp and Francis[11] have given an expression for the resonant charge transfer cross sections which is based on a simple nodeless wave function for the atomic valence electron. Although dependent on a number of simplifying assumptions, the predicted cross section is absolute in the sense that it is given only as a function of the velocity and ionization energy of the atom. The charge transfer cross sections calculated from this expression assuming the most probable thermal velocity are $2.6\text{x}10^{-14}$ cm^2 for Rb$^+$ and $3.1\text{x}10^{-14}$ cm^2 for Cs$^+$. To find the corresponding mobility cross sections, we must apply the correction[12] for the ion-induced dipole attraction, and multiply the result by two[10]

$$Q = 2\sigma' = 2\sigma[1 + (\alpha e^2/E\sigma^2)(\pi/2)^2] .$$

Here σ is the predicted charge transfer cross section, E is the average relative kinetic energy of the particles, α is the polarizability and e is the electron charge. The results are $6.5\text{x}10^{-14}$ cm^2 for rubidium, and $7.6\text{x}10^{-14}$ cm^2 for cesium. These are in surprisingly good agreement with the experimental values.

For both the cesium and rubidium systems the mobility of the molecular ion was independent of the chopping frequency and ion drift distance. This was also true for the atomic ions at the higher E/P_o values, shorter drift distances, and higher chopping frequencies. However, when the time between production and collection of the atomic ions was allowed to increase, eventually the apparent drift velocity began to increase. In the limit of long times between production and collection, the atomic ions appeared to have a drift velocity identical to that of the corresponding molecular ion. Thus if the atomic ions are not collected rapidly, they are converted to molecular ions, most probably by the exothermic reactions

$$Rb^+ + Rb_2 \longrightarrow Rb_2^+ + Rb \qquad (1)$$

$$Cs^+ + Cs_2 \longrightarrow Cs_2^+ + Cs \qquad (2)$$

Because the alkali metal vapors contain approximately 0.05% of diatomic molecules under our conditions, these reactions are expected to be considerably faster than the corresponding three body association processes. The approximate half-life for reactions 1 and 2 was estimated from the phase shift that corresponded to a measured drift velocity half-way between those expected for the atomic and molecular ions at a given E/P_o. To evaluate the bimolecular rate constants, the concentrations of the neutral diatomic molecules were calculated from the expressions for the equilibrium constant for molecule formation in terms of partition functions. The data tabulated by Wagman et al[13] were used to evaluate the partition functions. The second order rate constants for reactions 1 and 2 were found to be 8×10^{-10} and 9×10^{-10} cc/molecule-sec respectively. An approximate upper limit for the rate constants of such simple exothermic ion-molecule reactions can be calculated from the expression

$$k = 2\pi\left(\frac{\alpha e^2}{\mu}\right)^{1/2}$$

where α is the polarizability of the neutral, e is the fundamental charge, and μ is the reduced mass. If the polarizability for the molecule is taken as twice that of the atom, the rate constants calculated from this expression are 29×10^{-10} and 26×10^{-10} cc/molecule-sec for reactions 1 and 2 respectively. As expected, these calculated rate constant exceed our experimental estimates, but the two are reasonably close. It is clear from these rates that the occurrence of reactions 1 and 2 will limit the range of temperatures and pressures in which the monatomic alkali ions can be observed in their parent vapors.

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Table 1

Normalized Zero-field Mobilities

Rb^+	0.18 cm^2/V sec
Rb_2^+	0.29
Cs^+	0.12
Cs_2^+	0.20

Figure Captions

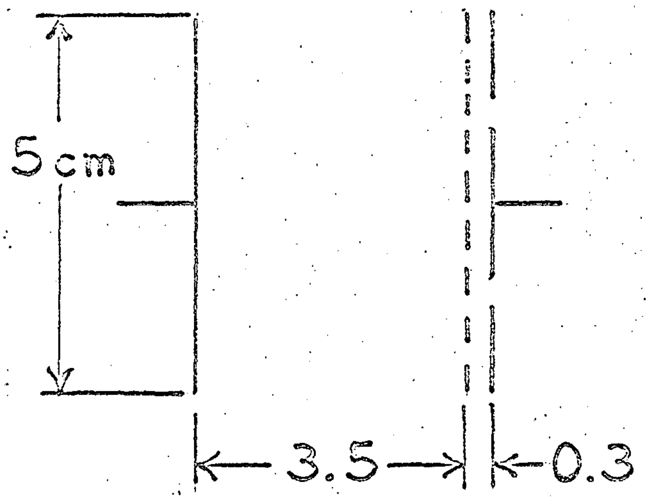
Fig. 1. Electrode arrangement in mobility cell.

Fig. 2. Drift velocity as a function of E/P_0 for ions in rubidium. Slopes of unity and one half are indicated.

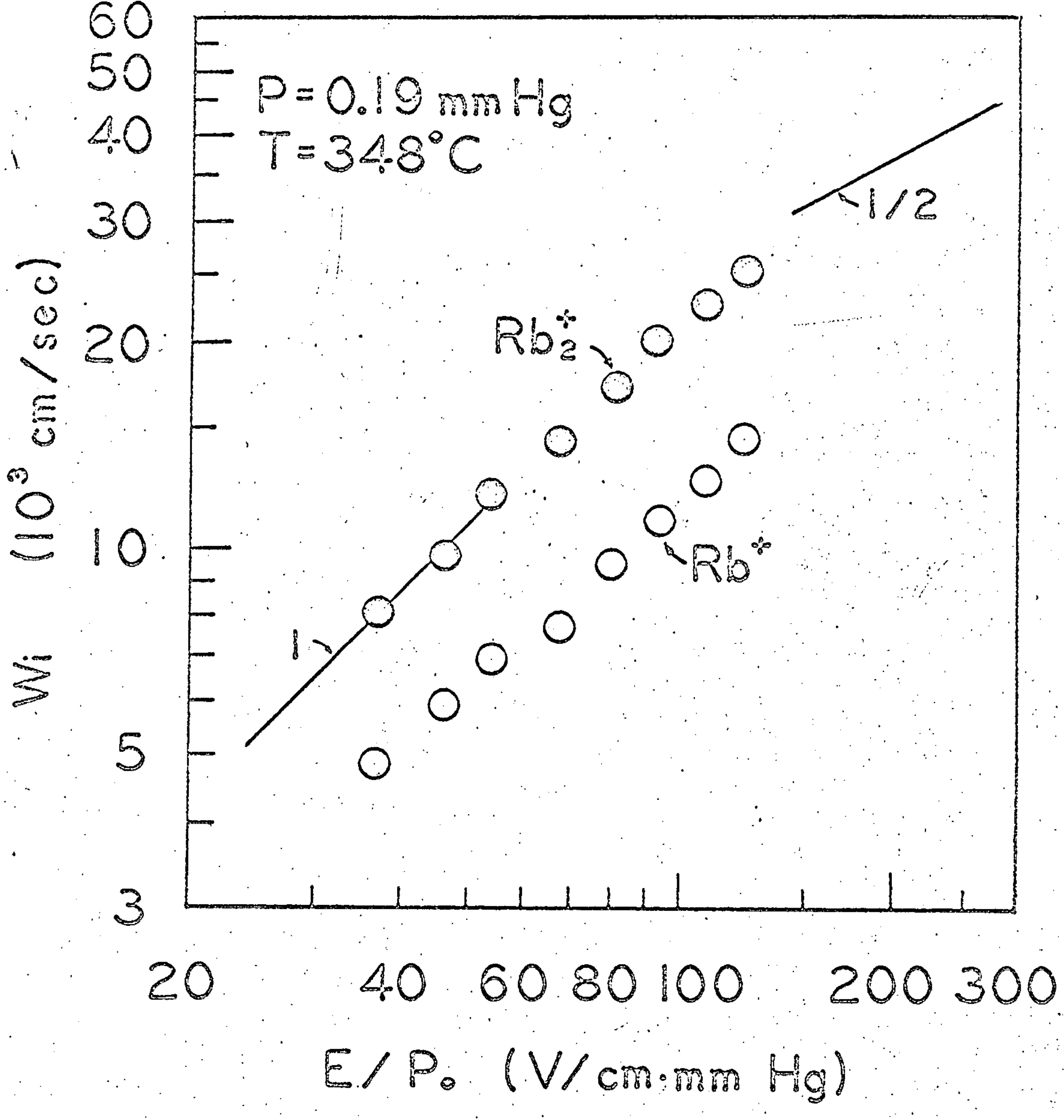
Fig. 3. Drift velocity as a function of E/P_0 for ions in cesium. Slopes of unity and one half are indicated.

Fig. 4. Normalized mobility as a function of E/P_0 for ions in rubidium.

Fig. 5. Normalized mobility as a function of E/P_0 for ions in cesium.



Lee & Mahan Fig 1



Lee + Mahan Fig 2

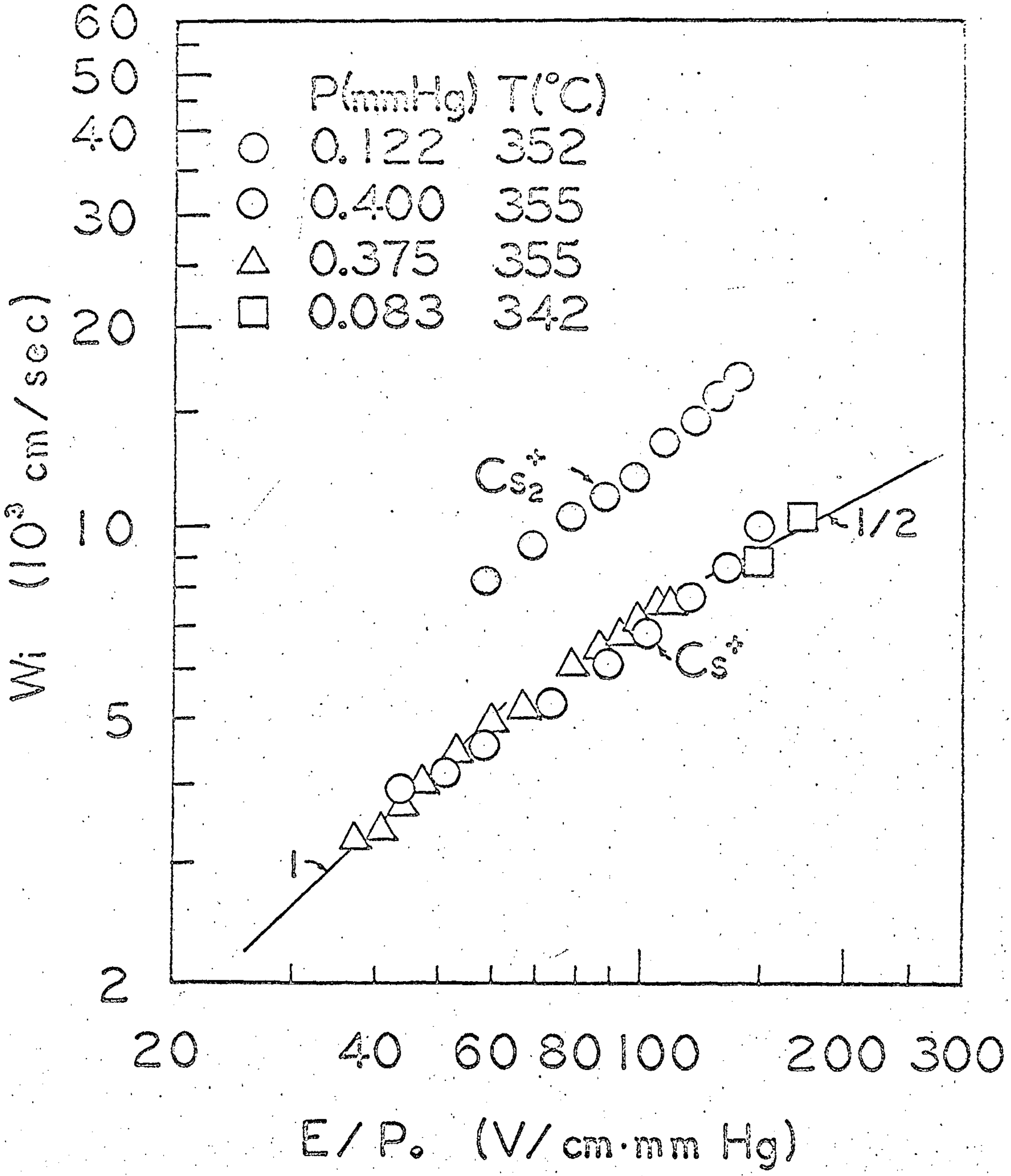
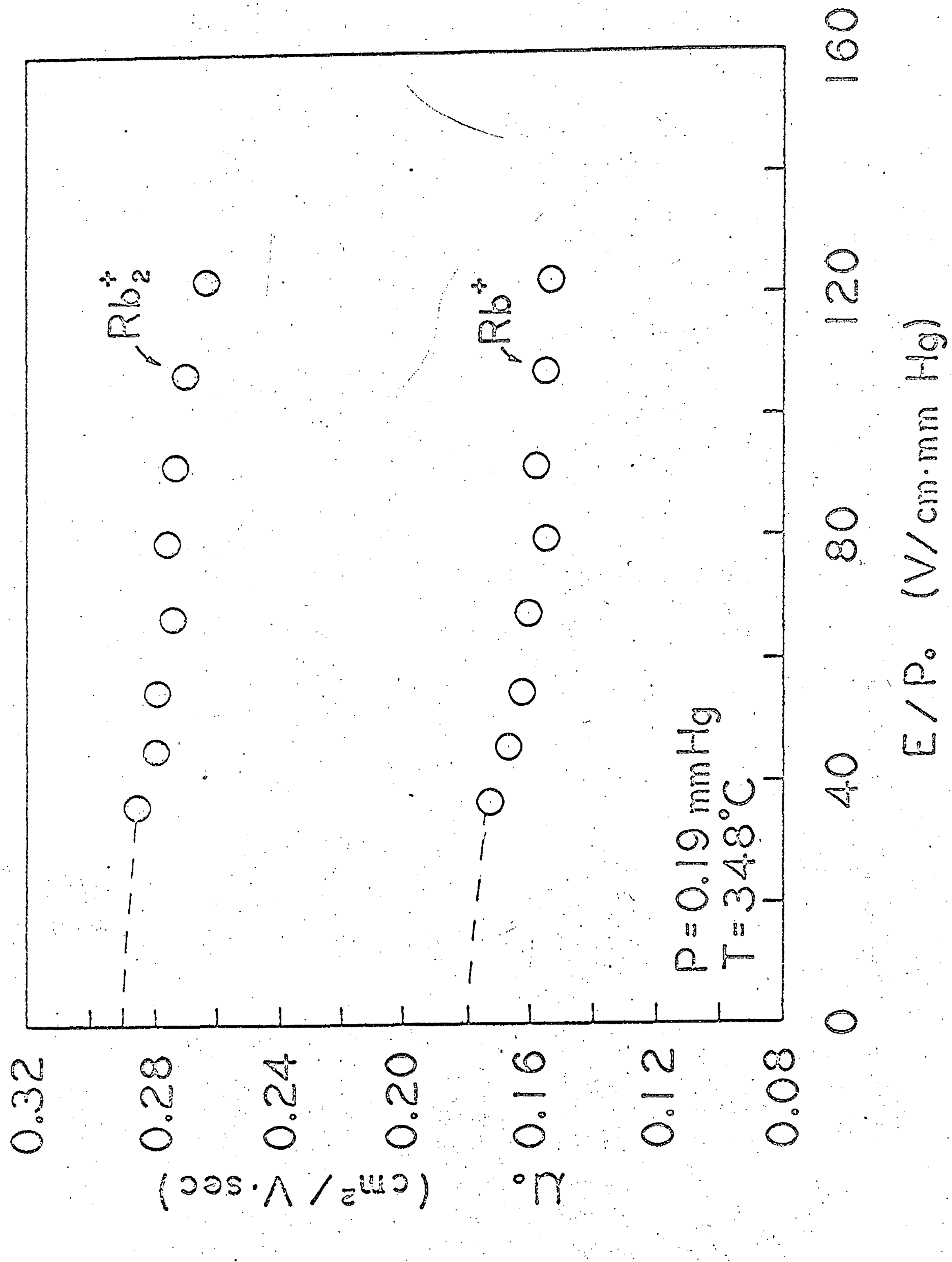
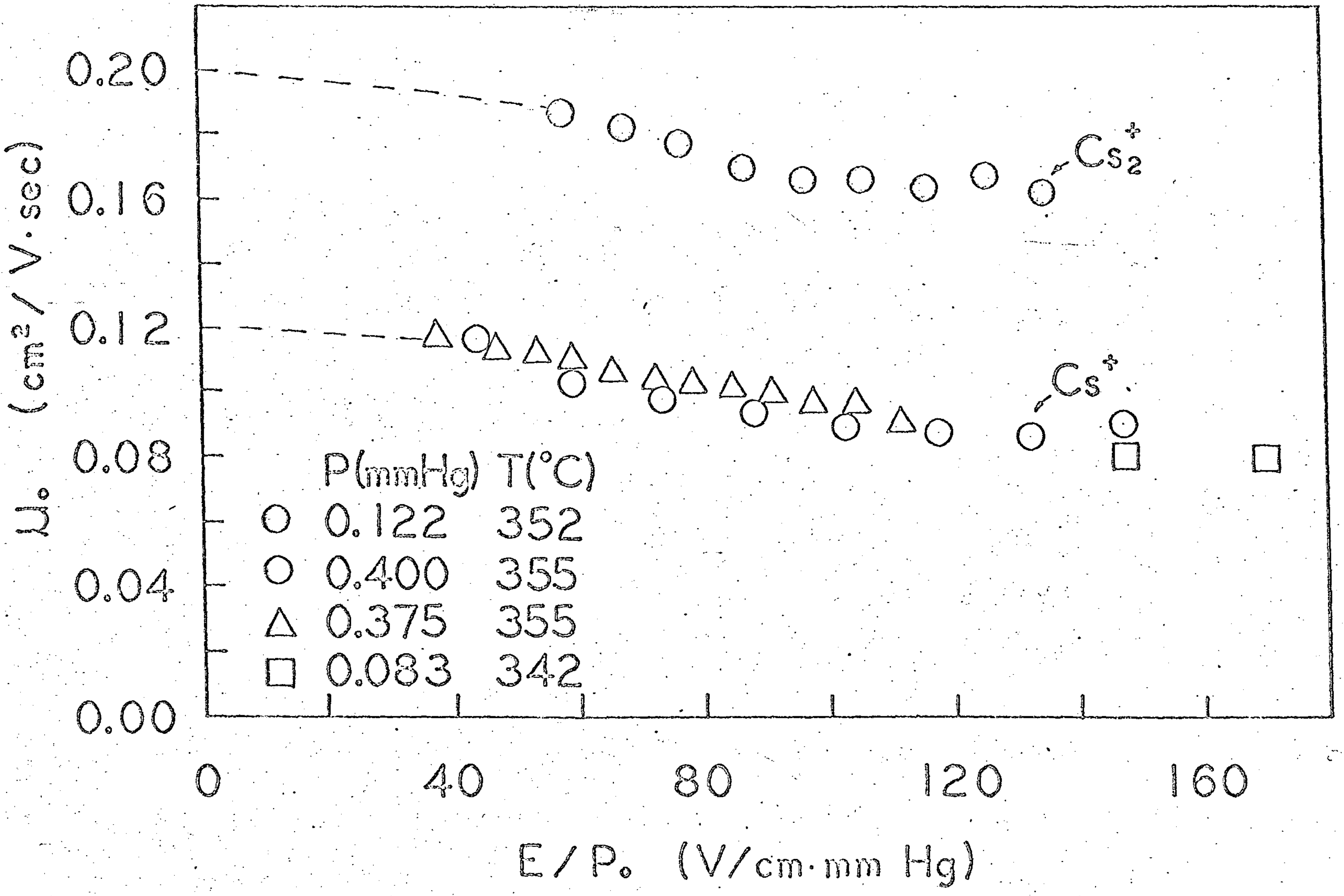

P(mmHg) T(°C)
○ 0.122 352
○ 0.400 355
△ 0.375 355
□ 0.083 342
Cs_2^+
Cs^+
1
1/2
Wi (10^3 cm/sec)
60
50
40
30
20
10
5
2
20
40
60
80
100
200
300
E/P₀ (V/cm·mm Hg)

Fig 3



Leo + Mahan Fig 4



Sent Mahan Fig 5