MOBILITIES OF MASS-IDENTIFIED ATOMIC IONS IN THE NOBLE GASES

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Prepared for:

Advanced Research Projects Agency
Army Research Office-Durham

June 1973

SPACE RESEARCH COORDINATION CENTER

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BY

R. JOHNSEN, M. T. LEU AND MANFRED A. BIONDI

SPONSORED BY
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ARPA ORDER NO. 826
CONTRACT NO. DA-31-124-ARO-D-440

MONITORED BY
U. S. ARMY RESEARCH OFFICE-DURHAM

SRCC REPORT NO. 189

JUNE 1973

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UNCLASSIFIED

Security Classification

AD 766276

DOCUMENT CONTROL DATA · R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a REPORT SECURITY CLASSIFICATION
University of Pittsburgh Pittsburgh, Pa. 15260	Unclassified
	2b GROUP

3 REPORT TITLE

MOBILITIES OF MASS-IDENTIFIED ATOMIC IONS IN THE NOBLE GASES

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Scientific paper - issued June 1973

5 AUTHOR(S) (Last name, first name, initial)

R. n.m.i. Johnsen, M. T. Leu and Manfred A. Biondi

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
June 1973	~~23~~ 26	30

8a CONTRACT OR GRANT NO	9a ORIGINATOR'S REPORT NUMBER(S)
DA-31-124-ARO-D-440 b. PROJECT NO. P-6563-P c ARPA Order 826, Am. 9 d	APP-41 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report) SRCC No. 189

10 AVAILABILITY/LIMITATION NOTICES

Approved for public release; distribution unlimited.

11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
MONITORED BY: U. S. Army Research Office-Durham	Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, Va. 22209

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DD FORM 1 JAN 64 1473

1a

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Positive Ion Mobilities Atomic Ions Drift/Tube/Mass Spectrometer						

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Mobilities of Mass-Identified Atomic Ions in the Noble Gases

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ABSTRACT

A drift tube/mass spectrometer apparatus has been used to determine the mobilities of mass-identified atomic ions in the noble gases as a function of E/p (drift field/gas pressure) at T = 295 K. The measured values of the reduced mobilities μ_o of He^+ in He, Ne^+ in Ne and Ar^+ in Ar are in agreement with earlier investigations which did not employ mass-identification. The measured value at E/p = 0, $\mu_o(H^+$ in He) = $(31.0\ ^{+\ 0.5}_{-\ 1.0})$ $cm^2\ V^{-1}\ sec^{-1}$, is in good agreement with quantal calculations, but the observed decrease of μ_o with ion energy is somewhat slower than that predicted by theory. The measured mobility of each of the noble gas ions Ne^+, Ar^+, Kr^+ and Xe^+ in He is found to be ~6-12% lower than that of the corresponding alkali ion (as determined by Tyndall's group).

I. INTRODUCTION

The experimental study of the mobilities of positive ions in various gases has provided information concerning the nature of ion-atom interatomic forces. This has been especially true where a related series of ions and/or atoms (e.g. alkali ions in noble gases[1-3]) has been investigated. Unfortunately, in a number of studies the identity of the ion under investigation has been in doubt, and therefore the measurements have contributed little to our basic understanding. The recent use of drift mobility tube/mass spectrometer apparatus to determine ion mobilities and ion-molecule reaction rates[4-8] has corrected this problem by providing a means for unambiguous identification of the ions under study.

We have applied an improved version of our mobility tube/mass spectrometer apparatus[9] to a determination of the mobilities of He^+ in He, Ne^+ in Ne and Ar^+ in Ar (ion-parent atom cases) and of H^+, Ne^+, Ar^+, Kr^+ and Xe^+ ions in He gas (unlike ion-atom cases) over the range from 295 K to ~0.4 eV ion-atom relative energy. While in the atomic ion-parent atom cases there is little need for mass spectrometric identification of the ions, in the unlike ion-atom studies, the possibility of complex ion formation in the gas mixtures (e.g., HeH^+ in hydrogen-helium) necessitates positive identification of the ions under study.

The atomic ion-parent atom measurements provide a check of our mobility determinations against well-established mobility values.[10] The study of the series of noble gas ions in helium permits a comparison with corresponding measurements of mobilities of alkali ions in helium[1-3] to investigate systematic differences between the two series. Finally, the determination of the mobility of H^+ in He permits a comparison with recent measurements[11-13] and *theoretical* calculations.[14]

II. METHOD OF MEASUREMENT

The mobility tube/mass spectrometer apparatus and the method of determining ion mobilities have been described in detail recently.[9] The apparatus consists of a pulsed electron bombardment ion source, a drift tube in which a uniform electric field is established by a series of guard rings, and a differentially pumped section containing a quadrupole mass spectrometer and a channeltron electron multiplier. A pulse of ions from the source enters on the axis of the drift section through a small (0.4 cm diam) injection orfice. (Small drawout voltages are applied in the ion source to minimize the ion injection energy.) The ions traverse the drift region, and those remaining on axis effuse through an exit orifice (0.046 cm diam) into the differentially pumped mass spectrometer. Individual ions are counted with the aid of a channeltron electron multiplier (gain $\sim 10^7$), and the ion counts are coherently summed over many cycle repetitions in a multichannel analyzer operating in a time-of-flight mode to determine the ion arrival spectrum.

The mobility is determined from measurements of the time required for the ions to transit the known length of drift region (the ~ 3 to 30 μsec transit time through the quadrupole spectrometer is subtracted from the measured time). The ion transit time is taken as the time of arrival of the maximum in the ion pulse at the exit orifice. Calculations[15] show that, in spite of diffusion broadening, the time of maximum signal is within ~1/2% of the actual transit time.

The small (~5%) inhomogeneity in the drift field near the entrance orifice can be shown to require only a second order and therefore negligible correction to the mobility determined from the equation

$$\mu = \frac{v_d}{E} = \frac{L^2}{V_{app}\, t_t} \quad , \tag{1}$$

where v_d is the ion drift velocity in the applied drift field E, V_{app} is the total voltage applied over the drift length $L(=15.75$ cm) and t_t is the ion transit time through the drift region.

Since we are unable to vary the length of the drift region, care must be taken to eliminate effects of ion injection at velocities exceeding the drift velocity. As described previously,[9] after injection the ion pulse is returned to the entrance plate (by reversing the drift field) where most of the ions are absorbed. The original drift field direction is restored and the ion transit time measured from this time origin. In practice, we have usually found negligible difference between the transit time so determined and that measured without field reversal when the drawout voltages in the ion source are kept small.

The mobilities are measured as a function of E/p, where p is the gas pressure, and the ions' mean energy of relative motion is calculated using an expression derived by Wannier[16] under the assumption of a constant mean free time between ion-atom collisions. According to his theory, the ion mean energy in the laboratory frame is given by

$$\bar{\varepsilon}_{lab} = \frac{3}{2}\, kT + \frac{1}{2}\, (M+m) v_d^2 \quad , \tag{2}$$

where M is the mass of the gas atom, m the mass of the ion, v_d the drift velocity, k Boltzmann's constant and T the gas temperature. From this, the mean energy of relative motion between the ion-atom collision pairs is readily shown to be:

$$\bar{\varepsilon} = \frac{3}{2}\, kT + \frac{1}{2}\, M\, v_d^2 \quad . \tag{3}$$

The assumption of a constant mean free time between collisions is appropriate in cases where the momentum transfer cross section varies inversely with velocity. Such a variation is encountered in the many cases where the principal interaction between ion and atom is of the point charge-induced dipole type. However, the assumption of a constant mean free time is poor in the case of ions drifting in their parent gas, where resonant charge transfer is usually the dominant interaction. As has been noted previously,[7] Wannier's formula tends to overestimate the ion mean energy by as much as a factor $4/\pi$ in this case.

III. RESULTS

A. Ion-Parent Atom Mobilities

The measured reduced mobilities μ_o of mass identified He^+ ions in helium at 295 K are shown by the upper set of data points in Fig. 1. (In keeping with current usage the mobilities are referred to a standard gas density of 2.69×10^{19} cm^{-3}.) Shown for comparison is the empirical analytic fit[17] (solid line) of the data of Beaty and Patterson[18] ($1.5 < E/p < 9.5$) and of Hornbeck[19] ($7.5 < E/p < 320$). This curve also fits the data of Biondi and Chanin[20] ($1.5 < E/p < 11$). However, it falls ~14% below the mass-analyzed data of Madsen, Oskam and Chanin[4] ($8 < E/p < 25$) at the high E/p end of their measurements

The results of our studies of Ne^+ in Ne at 295 K are shown by the lower set of data points in Fig. 1. The solid line is the empirical analytic fit[21] of the data of Beaty and Patterson[21] ($2 < E/p < 26$), of Biondi and Chanin[20] ($3 < E/p < 15$), and of Hornbeck[19] ($10 < E/p < 600$). The dashed line represent an earlier empirical analytic fit[22] (not valid at very low E/p) of the data of Biondi and Chanin and of Hornbeck.

The measured mobilities of Ar^+ in Ar at 295 K are shown by the data points in Fig. 2. The solid curve is Frost's empirical analytic fit[22] of the data of Biondi and Chanin[20] ($8 < E/p < 36$) and of Hornbeck[19] ($22 < E/p < 800$). The dashed curve represents the results of mass-identified studies by McAfee, Sipler and Edelson.[8]

B. Unlike Ion-Atom Mobilities

The measured mobilities at 295 K of H^+ in He are shown by the upper set of data points in Fig. 3. Data taken by the field reversal technique (to eliminate injection effects) are shown by the cross-type symbols, while those taken conventionally are represented by the closed symbols. At low helium pressures and high E/p the field reversal technique yields ~10% higher mobility values. The hydrogen pressures (3×10^{-3} to 4×10^{-2} Torr) required for H^+ ion generation were not always negligible compared to the helium pressures (0.3 - 1 Torr), necessitating up to 6% Blanc's Law[23] correction of the mobilities to correspond to the pure helium case. The solid line represents the direct measurements of H^+ in He and the dashed line properly scaled measurements of D^+ in He (see next section) of Orient[12,13] for mass identified ions.

Our measurements for Ne^+ in He are shown by the lower set of data points in Fig. 3. The Ne^+ ion generation was accomplished with a very small partial pressure of neon ($\leq 8 \times 10^{-4}$ Torr), assuring that the measurements refer to the mobility of Ne^+ ions in helium.

The mobilities at 295 K for the other noble gas ions, Ar^+, Kr^+, and Xe^+, in helium are shown in Fig. 4. Again, only very small partial pressures of argon ($\leq 6 \times 10^{-4}$ Torr), krypton ($\leq 7 \times 10^{-4}$ Torr), and xenon (1.3×10^{-4} Torr) were required for appropriate ion generation in the helium gas.

IV. DISCUSSION AND CONCLUSIONS

A. Ion-Parent Atom Mobilities

Resonant charge transfer is the dominant interaction which determines the ion mobilities in the cases He^+ in He, Ne^+ in Ne and Ar^+ in Ar. In such cases the momentum transfer cross section, σ_m, is calculated[24] to vary approximately as

$$\sigma_m = (A - B \ln v)^2 \quad , \tag{4}$$

where A and B are constants and v is the ion-atom relative velocity, leading to prediction of a mobility which varies roughly as $(\bar{\epsilon}_{ion})^{-1/2}$. Our data, shown in Figs. 1 and 2, show a somewhat slower decrease with relative energy than suggested by this simple theory, the discrepancy increasing as we go from helium to argon. Inclusion of polarization attraction corrections[25] (largest for argon) would lead to prediction of a slower falloff of mobility with energy.

Extrapolations of our data to E/p = 0 (thermal energy) yield values in quite satisfactory agreement with the experimental results of Biondi and Chanin[20] shown by the arrows on the ordinates of Figs. 1 and 2, i.e. $\mu_o(He^+, He) = 10.5$, $\mu_o(Ne^+, Ne) = 4.0$, and $\mu_o(Ar^+, Ar) = 1.6$. These values are, in turn, in agreement with theory.[24-27]

The decrease in $\mu_o(He^+, He)$ with increasing E/p found in the present experiment is slightly faster than that observed by Hornbeck[19] (upper solid line in Fig. 1). However, the present studies of the variation of $\mu_o(Ne^+, Ne)$ with E/p are in agreement with the data of Beaty and Patterson[21] (solid line in the lower half of Fig. 1) and of Hornbeck[19] (dashed line). In the studies of $\mu_o(Ar^+$ in Ar), the present results are in satisfactory agreement with the data of Biondi and Chanin[20] and of Hornbeck[19] (solid line in Fig. 2); however, they disagree with the mass-

identified ion results of McAfee et al.[8] (dashed line) by up to ~10%.

In the case of helium, the long-drift distance (~16 cm) employed in the present experiment ought to yield mobility values as trustworthy as those obtained by Hornbeck in a short Townsend avalanche drift tube. Very recent studies in a long, double-shutter drift section (~50 cm length) added to a flowing afterglow tube[28] yield $\mu_o(He^+, He)$ values which lie intermediate between Hornbeck's and our values.

In the case of argon, McAfee et al.[8] used several experimental techniques to determine $\mu_o(Ar^+, Ar)$. Their data from $28 < E/p < 40$, obtained with a Hornbeck-type drift tube (no mass analysis), lie closest to our results, while their mass-analyzed ion results differ from ours both at low E/p (< 20) where they used an rf ion source, thermalizing space and short drift space (~1 cm) and at higher E/p (> 50) where they employed a Townsend avalanche in a short drift space (≲ 1 cm). End effect corrections in these short drift space measurements should lead to larger experimental errors than in our studies.

In view of the magnitudes of the random and systematic errors estimated for the present experiment (~±2% and ±5%, respectively) and those of the other experiments discussed in the preceding paragraphs, we conclude that the mobilities of mass-identified He^+, Ne^+ and Ar^+ ions in their parent gases have been determined to an accuracy of ~±5% and that these values are in quite satisfactory agreement with the predictions of available theory.

A. Unlike Ion-Atom Mobilities

H^+ in He

The simplest of the unlike ion-atom systems which may be readily studied experimentally is $H^+ + He$. This two-electron diatomic system is

sufficiently simple that accurate calculations of its potential curves as a function of internuclear separation can be carried out on present-day computers. From these curves it is a straightforward matter to calculate ion-atom momentum transfer cross sections and ion mobilities;[14] therefore comparison of experimental determinations and accurate quantal calculations can now be made.

The measured values of the mobility of H^+ ions in He shown in the upper half of Fig. 3 extrapolate to an $E/p = 0$ value $\mu_o = (31.0 \begin{smallmatrix} + 0.5 \\ - 1.0 \end{smallmatrix})$ $cm^2\ V^{-1}\ sec^{-1}$, using the data in which ion injection effects are eliminated (cross-type points); these data show very little variation with increasing E/p.

Let us first compare these observations with predictions of classical (Langevin[29]) theory which assumes that a long-range, point ion-polarizable atom (dipole) attraction is the principal interaction, i.e.,

$$V(R) = -\alpha e^2/2R^4 \quad , \tag{5}$$

where V is the potential energy at an ion-atom separation R, α is the atomic polarizability and e the electronic charge. Since, with the bare proton, electron exchange effects are absent, the repulsion is shorter-ranged than usual, and hence the polarization attraction should largely determine the value of the ion mobility and its dependence on energy. In this limit, the predicted mobility, given by the formula[10]

$$\mu_o' \equiv \mu_o\, m_r^{1/2} = 35.9\, \alpha^{-1/2} \quad , \tag{6}$$

with the ion-atom reduced mass m_r expressed in amu and α in atomic units, is $\mu_o = 34.1\ cm^2\ V^{-1}\ sec^{-1}$. In addition, in this pure polarization limit the mobility is independent of ion energy.

An accurate quantal calculation of $\mu_o(H^+, He)$ has been carried out by Dickinson;[14] his result at 295 K, $\mu_o = 33.4$, is shown by the short heavy dash extending from the ordinate in Fig. 3. Further, his calculations indicate a ~6% decrease in μ_o as the temperature is doubled from 300 K to 600 K. While we have not carried out temperature variation studies, the observed decrease in μ_o of ~2% as the ion-atom relative energy is doubled is substantially slower than the theoretical prediction.

The data of Orient[12] for $\mu_o(H^+, He)$ are shown by the solid line in Fig. 3. Also, by using the dependence on reduced mass of ion and atom given in Eq. (6), we have scaled Orient's data[13] for D^+ ions in He (dashed line). The excellent agreement between the two curves indicates the validity of the mass-scaling law. (Our scaling is approximate, since at the same E/p, D^+ and H^+ ions attain slightly different energies.) The value $\mu_o = 31.8$ obtained by extrapolation to E/p = 0 is ~3% higher than our measured value. Thus, the experimental values are somewhat lower in absolute magnitude (by 5 to 7%) than the quantum theoretical prediction and vary more slowly with ion-atom relative energy ("temperature") than predicted.

The results of the present studies and those of Orient should remove the ambiguity concerning the correct value of $\mu_o(H^+, He)$. In a recent paper, Mellor[11] measured ion mobilities in helium +1% hydrogen mixtures using a glow discharge ion source followed by a thermalizing region and a double shutter drift space. He detected only a single ion transit time and found a value $\mu_o = 22$ cm^2 V^{-1} sec^{-1} at low E/p (~5), increasing to a value ~25 at E/p = 18. In a later experiment he used a quadrupole mass spectrometer to identify the ions drifting out of a similar ion source and concluded that H^+ was the probable ion in the mobility studies. While we have insufficient information to identify the ion(s) present in

Mellor's studies, we feel our results and those of Orient clearly rule out H^+, since in this case there are no internal energy state differences which would admit two different mobility values for the same ion.

Ne^+, Ar^+, Kr^+, Xe^+ in He

The measurements on noble gas ions in helium shown in Fig. 3 (lower) and Fig. 4 permit us to compare the mobility of a series of ions having a single electron missing from a closed shell with the well-known, earlier studies[1-3] of closed shell alkali ions in helium. While the mobility $\mu_o(Ne^+, He)$ shows a noticeable decrease with increasing energy (E/p), the mobilities of Ar^+, Kr^+, and to a lesser extent Xe^+ show the lack of dependence on energy expected in the pure polarization (Langevin) limit.

The results of our determinations of the mobilities at thermal energy (E/p = 0) of various ions in helium are compared with results of other studies in Fig. 5. In addition to the alkali ion mobilities (▲ points from Ref. 1; ▽ points from Refs. 2 and 3) we have shown the mobilities[9] of the heavy atomic ions Hg^+ and U^+. It will be seen that there is a rather weak dependence of mobility on ion mass, except for very light ions.

If polarization attraction is the principal interaction which determines the ion mobilities, then the mass-scaled mobility μ_o' defined in the Langevin equation, Eq. (6), should vary little from ion to ion. This comparison is made in Fig. 6, where it will be seen that the variation with ion mass is still quite evident. In addition, all the values of μ_o' (except for H^+) lie above the pure polarization value, 30.5, calculated from Eq. (6).

Inclusion of the short-range repulsive interaction between the ion and atom reduces the polarization attraction at longer range, and therefore

the mobility exceeds the pure polarization limit at certain temperatures,[10,29] in keeping with our observations. However, in order to obtain an accurate fit to the measured temperature dependence of the mobility of Li^+ in He, it has been found necessary to include an additional attractive interaction energy,[10] the dispersion energy resulting from the polarization of the ion, so that a more complete representation of the ion-atom interaction than Eq. (5) is

$$V(R) = (\text{Repulsion}) - A/R^4 - B/R^6 \quad . \tag{7}$$

The inclusion of the attractive R^{-6} term has the effect of reducing the ion mobility slightly.

The observation that the mobility of each of the noble gas ions is less than that of the neighboring alkali ion may be explained in terms of the effect of the R^{-6} term. At moderate ion-atom separations, the effect of the short range repulsive interaction should be small and comparable for both the noble gas ion and the corresponding alkali ion. However, the unfilled shell of the noble gas ion should be more highly polarizable than the closed shell of the alkali ion, so that the R^{-6} attractive term is larger for the noble gas ion.[30] As a result the mobility of the noble gas ion should be reduced somewhat more than that of the corresponding alkali ions, as observed.

The fact that μ_o' of H^+ falls even lower (slightly below the pure polarization limit) does not contradict this argument, since the H^+ - He interaction is quite different from the interactions in the above cases. The ion polarizability contribution to the R^{-6} term in Eq. (7) is obviously zero and, as noted earlier, the repulsion term is pure Coulomb in character and therefore very short ranged. In this case, a classical mobility calculation should yield a value very near the pure polarization

limit. Somewhat coincidentally, the quantal calculation[14] yields a value of μ_o' at 300 K which is ~2% below the pure polarization value. Both of these predictions are in reasonable agreement with our observations.

The authors are indebted to S. Geltman for helpful discussions of ion mobility theory.

References

*This research was supported, in part, by the Advanced Research Projects Agency of the Department of Defense and was monitored by the U. S. Army Research Office-Durham under Contract No. DA-31-ARO-D-440.

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FIGURE CAPTIONS

Fig. 1. Reduced mobilities, μ_o, as a function of E/p and of mean energy of relative motion $\bar{\varepsilon}$ for He^+ in He and Ne^+ in Ne at T=295 K. The mean energies are referred to $\bar{\varepsilon}_{th}$ = 3/2 kT = 0.038 eV. Helium pressures: X, 0.21 Torr; □, 0.54 Torr. Neon pressures: Y, 0.15 Torr; + 0.42 Torr; Δ, 0.63 Torr; O, 1.04 Torr. See text for explanation of the various curves in the figure.

Fig. 2. Reduced mobilities as a function of E/p and of $\bar{\varepsilon}$ for Ar^+ in Ar at 295 K. Argon pressures: ●, 0.11 Torr; +, 0.60 Torr. See text for explanation of the solid and dashed curves.

Fig. 3. Reduced mobilities of H^+ and Ne^+ in He at 295 K. Helium pressures in H^+ studies: Y, 0.30 Torr; X, 0.66 Torr; +, 0.88 Torr; ▽, 0.38 Torr; □, 0.86 Torr; O, 0.97 Torr. Helium pressures in Ne^+ studies: +, 0.48 Torr; Δ, 0.84 Torr; X, 0.96 Torr. See text for explanation of various curves in the figure.

Fig. 4. Reduced mobilities of Ar^+, Kr^+, and Xe^+ in He at 295 K. Helium pressures in Ar^+ studies: □, 0.33 Torr; X, 0.42 Torr; +, 0.57 Torr; ●, 0.90 Torr. In the Kr^+ studies: +, 0.48 Torr; ●, 0.89 Torr. In the Xe^+ studies: □, 0.43 Torr; +, 0.68 Torr; ●, 0.96 Torr.

Fig. 5. Reduced mobilities of various ions as a function of ion mass at T ~ 300 K. The solid and open circles represent the present results; the other symbols represent measurements by other investigators (see text for references).

Fig. 6. Mass-scaled reduced mobilities, $\mu_o' = m_r^{1/2} \mu_o$, as a function of ion mass. The dot-dashed curve at μ_o' = 30.5 represents the predicted value in the limit of pure induced dipole attraction between ion and atom. The symbols are as in Fig. 5.

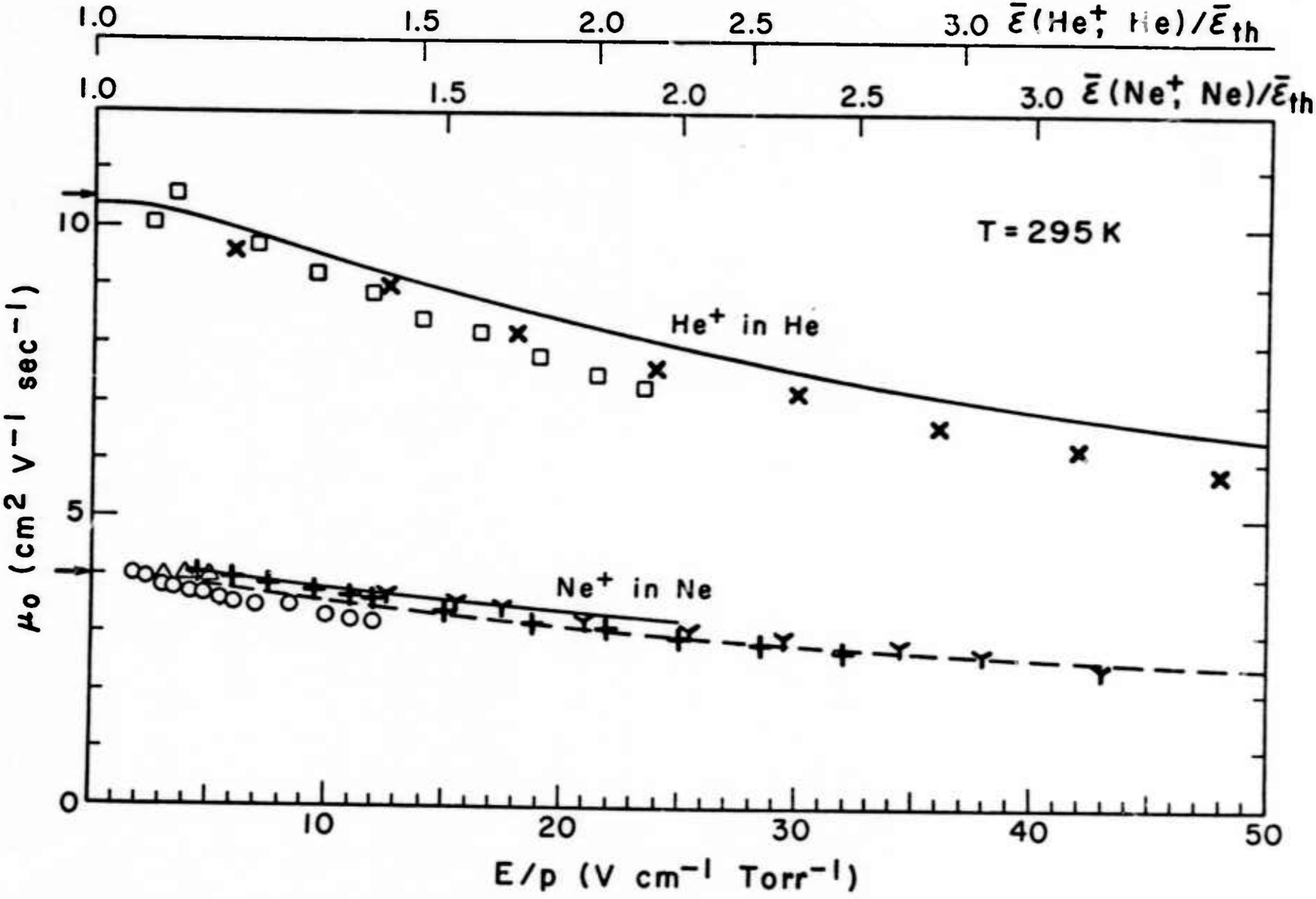
1.0
1.5
2.0
2.5
3.0 $\bar{\varepsilon}(He^+, He)/\bar{\varepsilon}_{th}$
1.0
1.5
2.0
2.5
3.0 $\bar{\varepsilon}(Ne^+, Ne)/\bar{\varepsilon}_{th}$
T = 295 K
He^+ in He
Ne^+ in Ne
μ_o (cm^2 V^{-1} sec^{-1})
10
5
0
10
20
30
40
50
E/p (V cm^{-1} Torr^{-1})

Figure 1

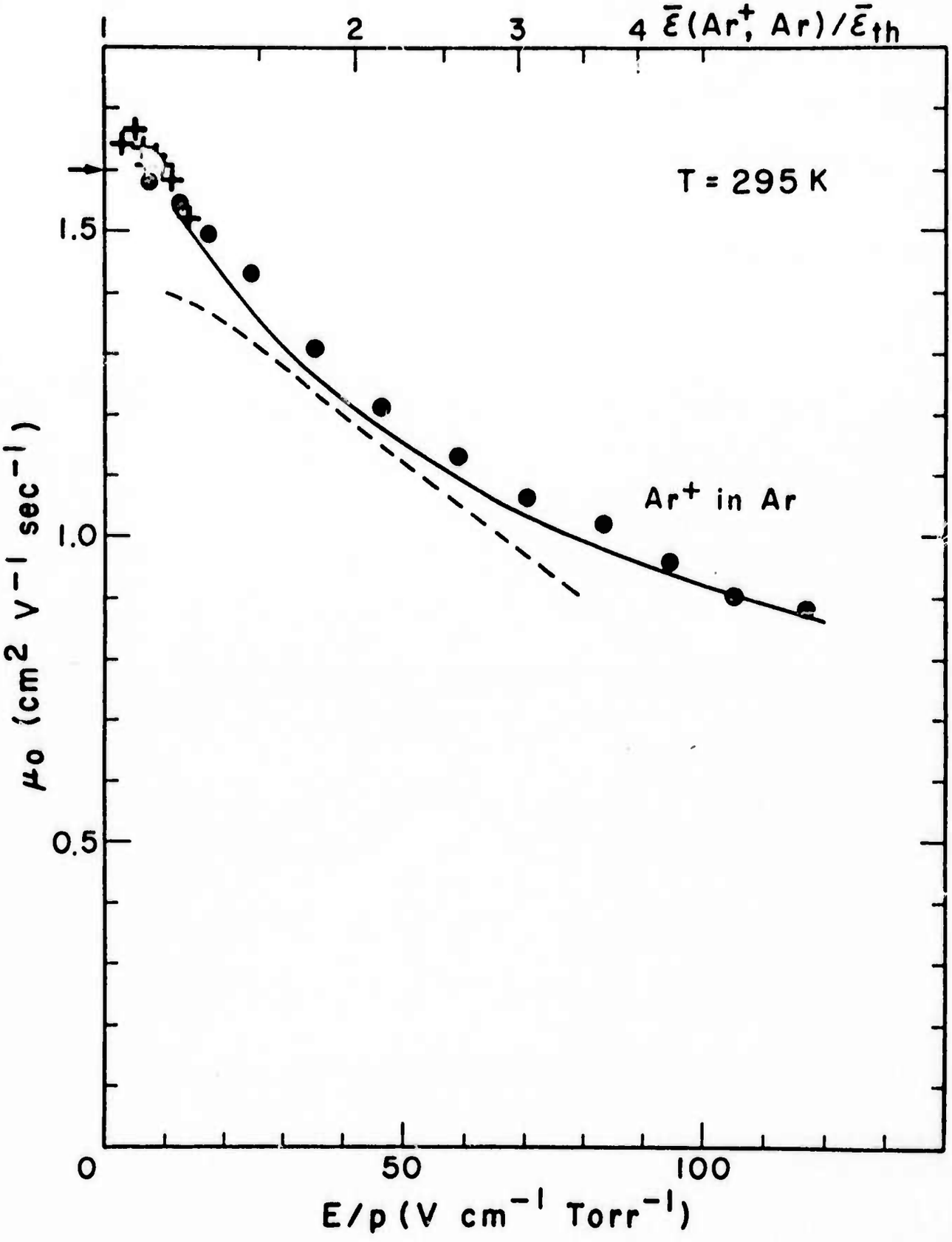
1
2
3
4 $\bar{\varepsilon}(Ar^+, Ar)/\bar{\varepsilon}_{th}$
T = 295 K
Ar^+ in Ar
μ_o (cm^2 V^{-1} sec^{-1})
1.5
1.0
0.5
0
50
100
E/p (V cm^{-1} $Torr^{-1}$)

Figure 2

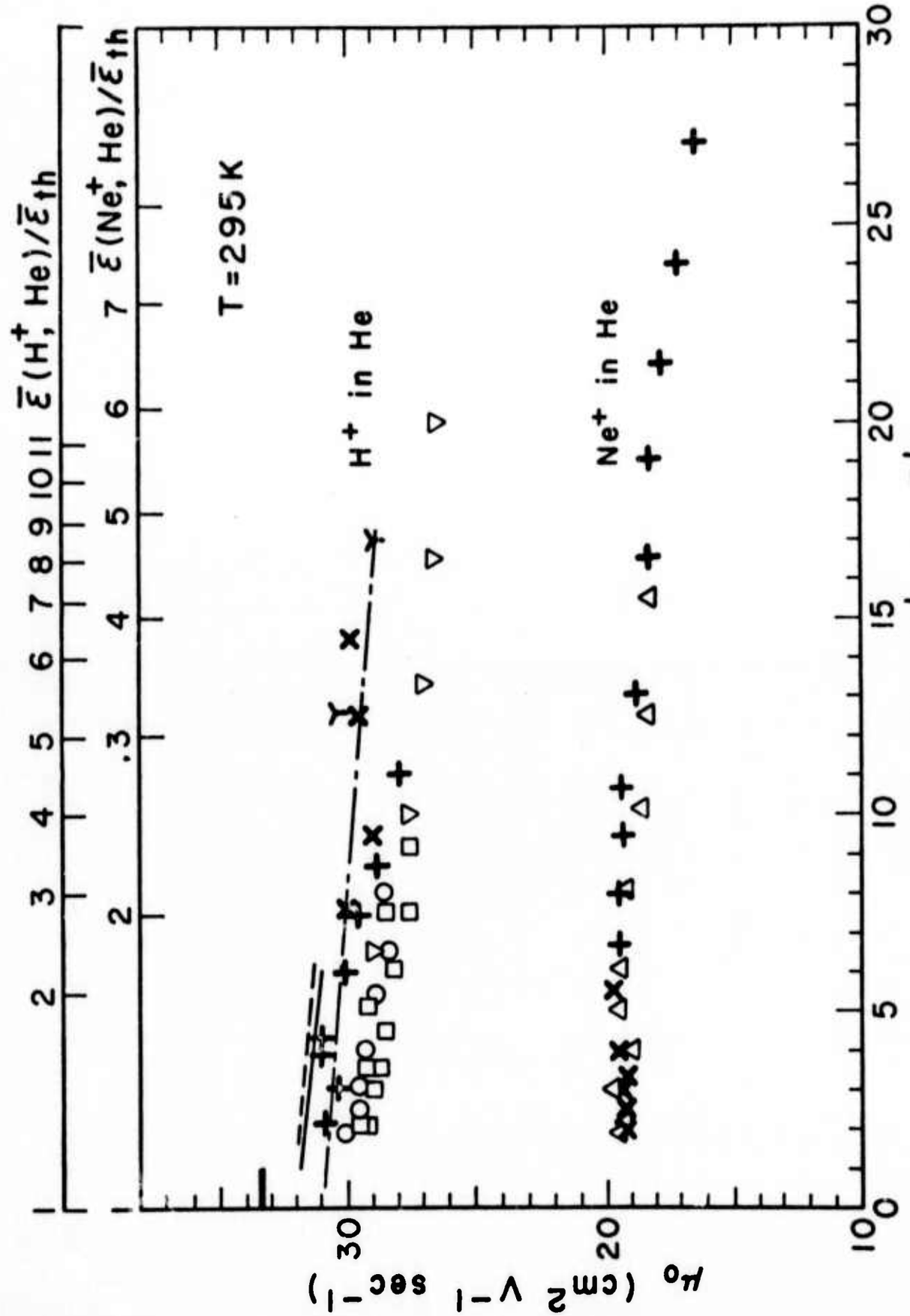
T=295 K
H+ in He
Ne+ in He
E/p (V cm-1 Torr-1)
μ0 (cm2 V-1 sec-1)
Ē(H+, He)/Ēth
Ē(Ne+, He)/Ēth

Figure 3

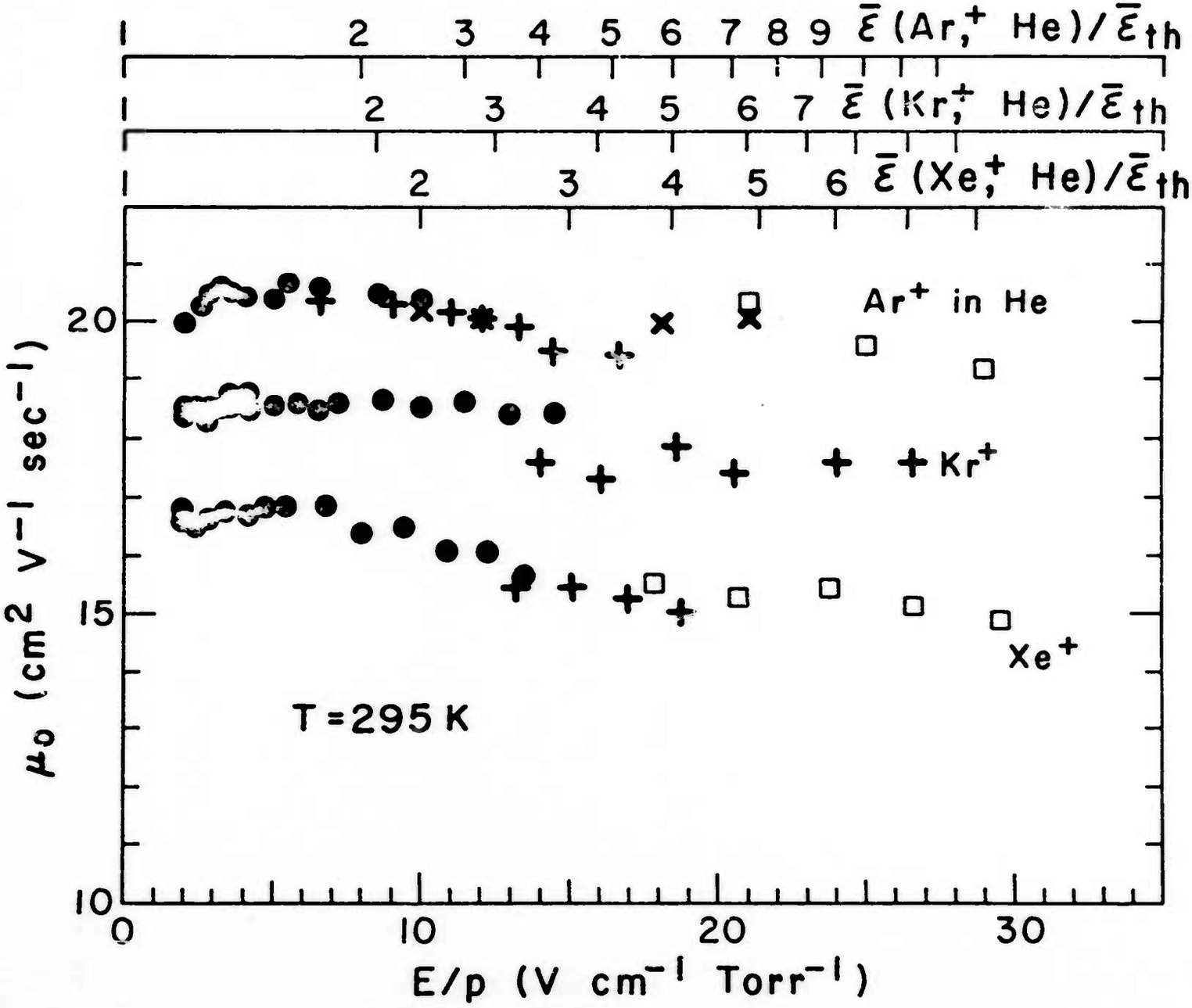
2 3 4 5 6 7 8 9 $\bar{\varepsilon}$ (Ar,+ He)/$\bar{\varepsilon}_{th}$
2 3 4 5 6 7 $\bar{\varepsilon}$ (Kr,+ He)/$\bar{\varepsilon}_{th}$
2 3 4 5 6 $\bar{\varepsilon}$ (Xe,+ He)/$\bar{\varepsilon}_{th}$
μ_0 (cm^2 V^{-1} sec^{-1})
20
15
10
Ar+ in He
Kr+
Xe+
T=295 K
0
10
20
30
E/p (V cm^{-1} Torr^{-1})

Figure 4

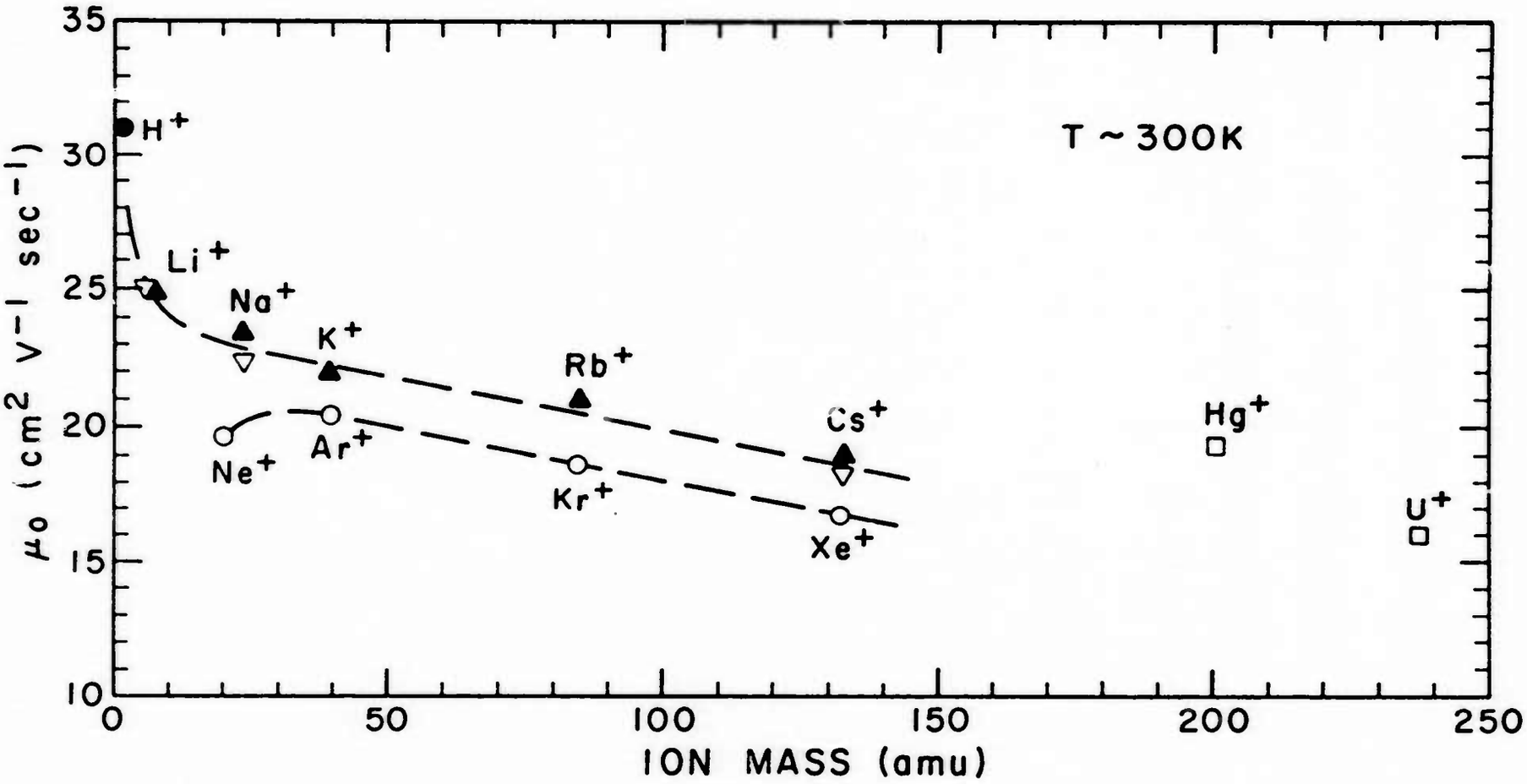
T ~ 300K
μ_o (cm^2 V^{-1} sec^{-1})
ION MASS (amu)
H+
Li+
Na+
K+
Rb+
Cs+
Ne+
Ar+
Kr+
Xe+
Hg+
U+
35
30
25
20
15
10
0
50
100
150
200
250

Figure 5

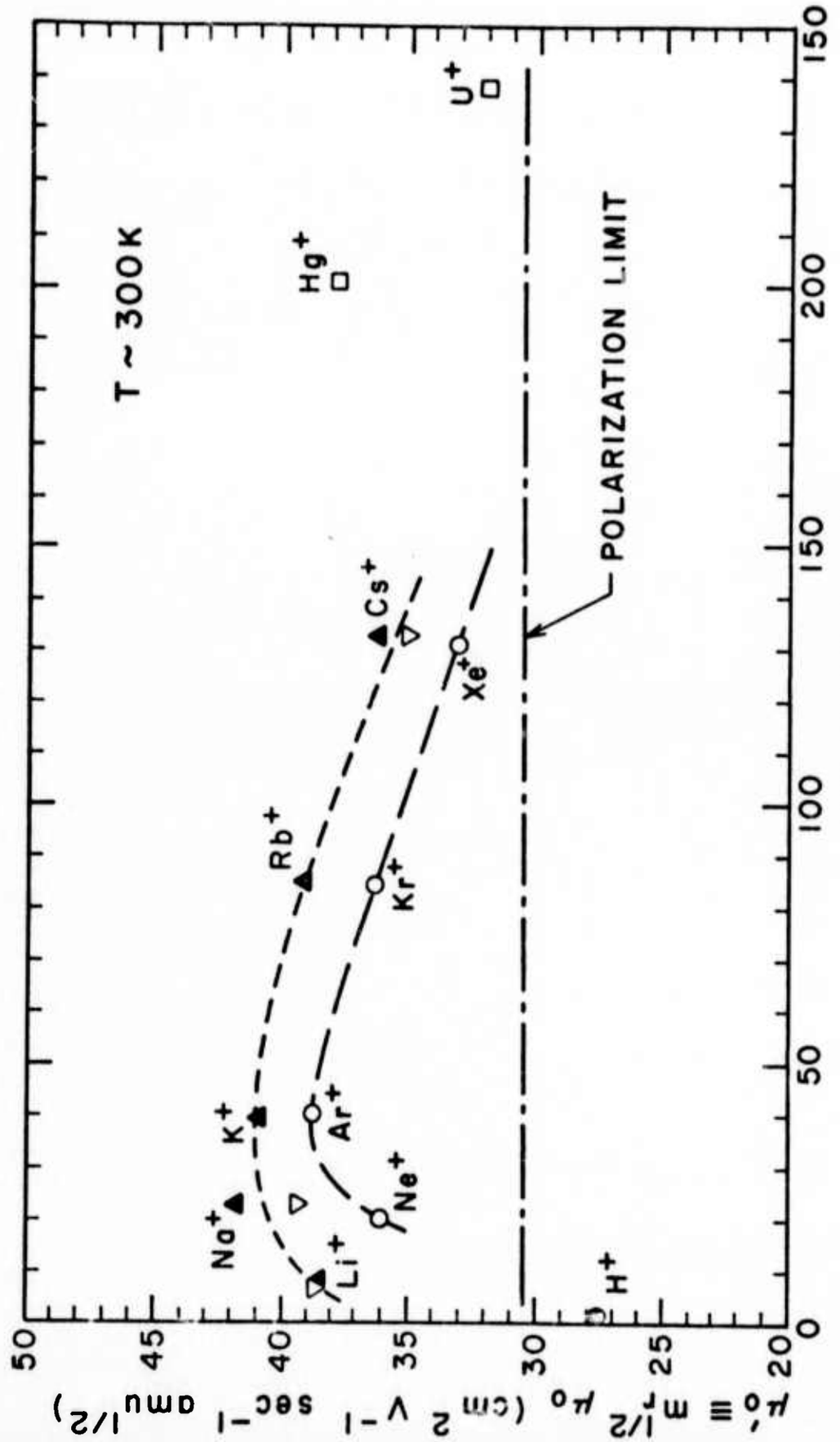
T ~ 300K
POLARIZATION LIMIT
ION MASS (amu)
$\mu_o' \equiv \mu_o^{1/2}$ ($cm^2\ V^{-1}\ sec^{-1}\ amu^{1/2}$)
Li+
Na+
K+
Rb+
Cs+
H+
Ne+
Ar+
Kr+
Xe+
Hg+
U+
0
50
100
150
200
20
25
30
35
40
45
50

Figure 6