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Charge transfer of $Ar^+ + N_2 \rightleftarrows N_2^+ + Ar$ at near thermal energies

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In a drift experiment, results have been obtained on the energy dependences of the rate coefficients for the forward and reverse reaction $Ar^+(^2P_{3/2}) + N_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ar + N_2^+$ ($v = 0$ and $v \neq 0$). The forward reaction predominantly proceeds via an endoergic channel, resulting in the ionic product $N_2^+(X, v \neq 0)$, and k_f increases from 1×10^{-11} cm^3 sec^{-1} to 7×10^{-10} cm^3 sec^{-1} in the energy range from thermal up to $E_{c.m.} \sim 3$ eV. In the reverse direction the reaction is fast in the entire energy range investigated (a few tenths of an eV up to about 6 eV) for vibrationally excited N_2^+, for which the reaction is exoergic, but it shows a strong energy dependence in the case of $N_2^+(v = 0)$, reflecting the endoergicity of this reaction path.

I. INTRODUCTION

The values of rate coefficients of ion molecule reactions obtained with different well-established techniques, e.g., flowing afterglows,[1-3] drift tubes,[4-6] stationary afterglows,[7-9] or ion cyclotron resonance,[10,11] generally agree to within ±30%. Thus the majority of values obtained in different laboratories lie well within the combined error limits of the various methods used. There is one rare example, the reaction

$$Ar^+ + N_2 \xrightarrow{k_f} N_2^+ + Ar\,, \qquad (1)$$

for which the reported thermal rate coefficients scatter over nearly two orders of magnitude from $k_f = 1 \times 10^{-12}$ cm^3 sec^{-1} to 6.6×10^{-11} cm^3 sec^{-1}, as can be seen from Table I. The highest values were obtained by Warneck,[18] who used a photoionization mass spectrometer, and by Laudenslager *et al.*,[10] using the ion cyclotron resonance (ICR) technique. Among the values measured with afterglow techniques, those obtained in an Ar buffer are the lowest ones. Adams *et al.*[16] investigated the reactions of Ar^+ with H_2, O_2, and N_2 in a flowing afterglow using a helium buffer with Ar admixed in various amounts up to some 10%. While the admixture of Ar to helium buffer had no effect on the observed coefficients of the reactions of Ar^+ with H_2 and O_2, the one for $Ar^+ + N_2$ dropped from 1.0×10^{-11} to about 4×10^{-12} cm^3 sec^{-1} when the Ar density was increased from zero to 2×10^{15} cm^{-3} and this effect was observed independently of the He buffer pressure, which was varied from 0.4 to 2.5 torr. This fact might have indicated the possible influence of a back reaction

$$N_2^+ + Ar \xrightarrow{k_r} Ar^+ + N_2\,, \qquad (2)$$

but due to the lack of a convincing positive evidence for the occurrence of reaction (2) such an influence was disregarded. A trend to higher values of k_f with declining Ar pressure also was observed in a stationary afterglow experiment by Adams *et al.*[14] Drift tube measurements performed in a helium buffer by Kaneko *et al.*[17] and Thomas *et al.*[13] show a strong increase of k_f with increasing relative kinetic energy $E_{c.m.}$ of the reactants from about 1.2×10^{-11} cm^3 sec^{-1} at thermal energy to several 10^{-10} cm^3 sec^{-1} at $E_{c.m.} \sim 1$ eV. The

TABLE I. Rate coefficients for reaction of Ar^+ with N_2 obtained at about 300 K, all in units of 10^{-11} cm^3 sec^{-1}. DC = discharge; DT = drift tube; ICR = ion cyclotron resonance method; SA = stationary afterglow; FA = flowing afterglow; PIMS = photoionization mass spectrometer.

Rate coefficient	Buffer gas	Year of publication	Method	Authors
0.2–1.5	Ar	1978	DC	Howorka (Ref. 12)
1.2	He	1978	DT	Thomas *et al*. (Ref. 13)
2.2		1974	ICR	Laudenslager *et al.* (Ref. 10)
0.1–0.4	Ar	1972/73	SA	Adams *et al*. (Ref. 14)
0.25	Ar	1971	FA	Hyatt *et al*. (Ref. 15)
0.4–1.0	He-Ar	1970	FA	Adams *et al*. (Ref. 16)
1.3	He	1969	DT	Kaneko *et al*. (Ref. 17)
6.6		1967	PIMS	Warneck (Ref. 18)
0.6	He-Ar	1966	FA	Fehsenfeld *et al*. (Ref. 19)

drift tube values[13,17] obtained at room temperature also agree well with the flowing afterglow values of Adams *et al.*,[16] obtained in a pure-helium buffer, where no influence of a back reaction (2) is possible.

Thus a room-temperature value of $k_f \cong 1 \times 10^{-11}$ $\mathrm{cm^3\,sec^{-1}}$ seems to be reasonable and a very recent measurement performed by Smith and Adams[20] using a selected ion flow tube (SIFT) technique confirms this value (see accompanying paper[20]).

Despite the many conflicting data of k_f published in the literature, so far no detailed investigations have been reported on the endoergic back reaction (2), which might have led to an understanding of the strongly differing values k_f. In the present investigation we performed measurements on the forward as well as on the reverse reaction (1) and (2), respectively, in the energy range from $E_{\mathrm{c.m.}} = 0.1$ to a few eV using a helium-buffered drift tube, and also obtained values for k_r from thermal energies up to 0.5 eV from equilibrium data in Ar-N_2 mixtures.

II. EXPERIMENTAL

The drift apparatus used for the present investigation has been described in detail in the literature[6] and hence only a brief summary of the specifications important in this study needs to be given here. The system consists of a slow-flow drift tube, which is geometrically separated from the ion source, so that changes in the gas composition in the drift tube do not change the ion source conditions. Ions produced in a hollow cathode ion source are extracted through the sampling orifice ($\phi \leq 100$ μm) of a hole probe into a drift tube region of 15.8-cm length. After passing through the drift region, part of the ions entering a quadrupole system are mass analyzed and counted. A constant flow of buffer gas through the drift tube is maintained at a small enough rate, so that the drift velocity of the ions is always high relative to the bulk flow velocity of the buffer gas through the drift section. Addition of reactant gas to the buffer causes a decline of the count rate of reactant ions from which the rate coefficient of the reaction can be calculated in the usual way.[6]

At a certain E/N, where E is the electric field strength and N the buffer gas density in the drift section, the mean kinetic energy of the ions is given by the Wannier formula,[21]

$$E_{\mathrm{ion}} = \tfrac{1}{2} m v_d^2 + \tfrac{1}{2} M_b v_d^2 + \tfrac{3}{2} kT \,, \tag{3}$$

where T and M_b are the temperature and the mass of the buffer gas atoms, v_d and m the drift velocity and mass of the reactant ion and k denotes the Boltzmann constant. From the Wannier expression the relative kinetic energy $E_{\mathrm{c.m.}}$ is obtained as described by McFarland *et al.*[5] The drift velocities necessary to calculate the rate coefficients and the $E_{\mathrm{c.m.}}$ values were obtained from Refs. 22 and 23.

For the measurement of the forward reaction (1) the hollow cathode discharge was operated in pure argon and for the reverse reaction (2) in pure nitrogen at a few hundredths of a torr and discharge currents of a few mA. Several checks of reactions (1) and (2) were carried out using a simple electron impact ion source operating with variable electron energy. The buffer gas temperature in the drift tube was kept at 296 K with the helium pressure varying in the range from 0.13 to 0.85 torr. A set of equilibrium constants $K = k_f/k_r$ was also obtained in Ar-N_2 mixtures at various E/N values, the necessary details of which are described below. The error limits of the rate coefficients obtained here are within ±30%, if not stated otherwise.

III. RESULTS AND DISCUSSION

A. The forward reaction $Ar^+ + N_2 \xrightarrow{k_f} N_2^+ + Ar$

The present results for k_f are shown in Fig. 1, together with the flowing afterglow value measured in a helium buffer by Adams *et al.*[16] at 280 K. A recent investigation with a temperature variable SIFT, performed by Smith and Adams[20] confirms this value and even shows the rate coefficient to decrease further with decreasing temperature to a minimum value of 8×10^{-12} $\mathrm{cm^3\,sec^{-1}}$ at 140 K but then again to increase to about 1×10^{-11} $\mathrm{cm^3\,sec^{-1}}$ at 80 K.

Data obtained in a drift experiment by Thomas

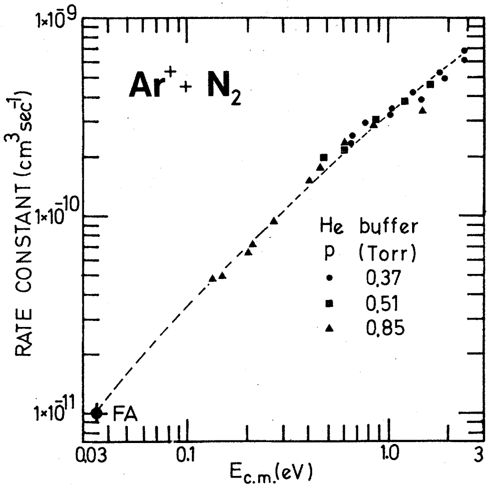

FIG. 1. Energy dependence of the rate coefficient for the charge-transfer reaction of Ar^+ with N_2. FA denotes an earlier flowing afterglow result obtained at 280 K by Adams *et al.* (Ref. 16).

et al.[13] for this reaction in the energy range from thermal up to about 1 eV are slightly higher than the present ones, but well within the combined error limits of the two experiments. There is excellent agreement between the present set of data and yet unpublished results[24] obtained in a flow-drift tube.

As the Ar^+ ions are produced by electron impact in the hollow cathode discharge both states Ar^+ $(^2P_{1/2})$ and Ar^+ $(^2P_{3/2})$ are assumed to be present in abundances determined by their statistical weights of 1 : 2.

The recombination energies of the two Ar^+ states differ by 0.18 eV (see Table II). While in the case of reactions of Kr^+ and Xe^+ different reactivities have been observed for the two spin states $^2P_{1/2}$ and $^2P_{3/2}$, respectively,[25] no such difference was evident for Ar^+ reactions,[10] and also in the present investigation only one decline was obtained for the Ar^+ signal at each E/N where measurements were performed. This indicated either the same reactivity for both states when reacting with N_2 or a fast quenching rate k_q for the conversion of Ar^+ $(^2P_{1/2})$ into Ar^+ $(^2P_{3/2})$ in collisions with N_2,

$$Ar^+(^2P_{1/2}) + N_2 \xrightarrow{k_q} Ar^+\,(^2P_{3/2}) + N_2\,. \qquad (4)$$

In this case the observed charge-transfer rate coefficient (Fig. 1) would be the one for the reaction

$$Ar^+\,(^2P_{3/2}) + N_2 \rightarrow N_2^+ + Ar\,. \qquad (5)$$

This is a likely explanation in view of recent results on Kr^+ and Xe^+ reactions obtained by Adams *et al.*,[25] which indicate that the $^2P_{3/2}$ states in general react faster than the $^2P_{1/2}$ states in reactions with molecular reactants. Thus the absence of a second, slower decline in the present study and in the above-mentioned earlier investigations may indicate a fast quenching rate coefficient k_q.

The observed strong increase of k_f with the relative kinetic energy of the reactants $E_{c.m.}$ may explain the high values of k_f obtained in the ICR experiment of Laudenslager *et al.*[10] and in the photoionization mass-spectrometer (PIMS) experiment of Warneck[18] (see Table I). Recent comparisons of flow-drift tube and ICR data[26] indicated the ions in the ICR experiment to have greater than thermal energies and it is also obvious that in the PIMS experiment the ion energies were considerably higher than the thermal ones. The lower val-

TABLE II. Recombination energies of Ar^+ and N_2^+ $(X^2\Sigma_g^+,\ v=0,1,2)$ in eV.

Ar^+		N_2^+ $(X^2\Sigma_g^+)$	
$^2P_{1/2}$	15.94	$v=2$	16.11
$^2P_{3/2}$	15.76	$v=1$	15.85
		$v=0$	15.58

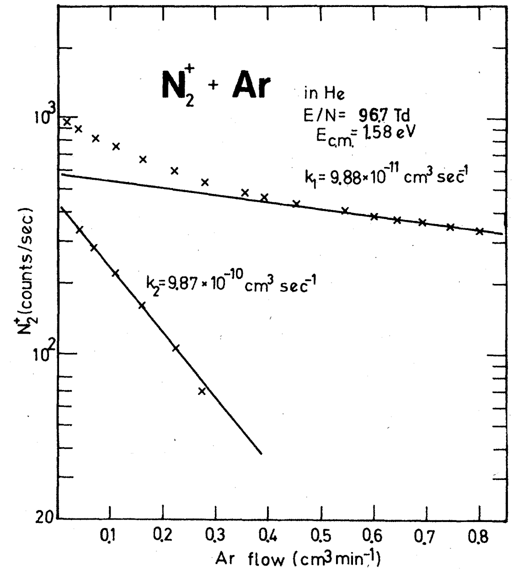

FIG. 2. Typical set of raw data for the reaction of N_2^+ with Ar. Addition of Ar to the helium buffer leads to a decline of the N_2^+ ion signal which is the sum of two exponential decays indicating the presence of excited N_2^+ besides N_2^+ $(X, v=0)$.

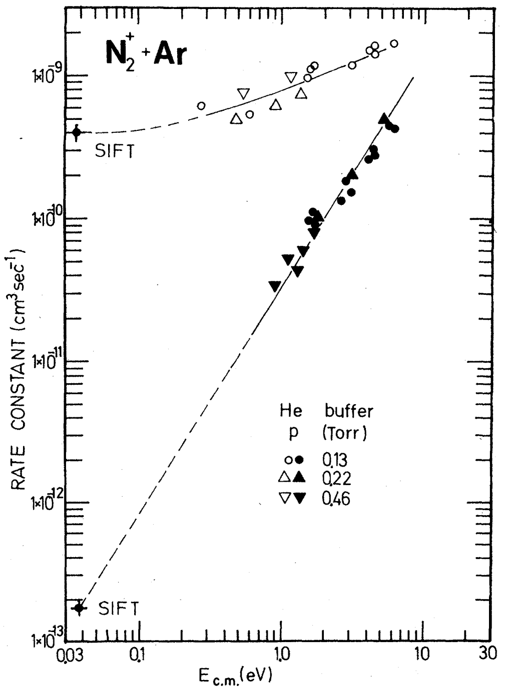

FIG. 3. Energy dependences of the reactions of N_2^+ $(X, v \neq 0)$ and of N_2^+ $(X, v=0)$ with Ar, denoted by open and full symbols respectively. Also shown are recent SIFT results, obtained from Ref. 20.

ues for k_f obtained in the experiments shown in Table I using Ar as a buffer or He-Ar mixtures may be partially explained by the data on the backward reaction (2) and on the equilibrium data shown below.

B. The reverse reaction $N_2^+ + Ar \xrightarrow{k_r} Ar^+ + N_2$

In the present work this reaction also was investigated in a helium buffer, in the energy range from a few tenths of an eV up to several eV. A typical set of raw data is shown in Fig. 2. With the addition of argon as a reactant gas, the N_2^+ ion signal showed two exponential decays in each case, from which two rate coefficients were calculated, a large one, which we attribute to the $N_2^+ (X, v > 0)$ states, and a small one, most likely the one due to the $N_2^+ (X, v = 0)$ state. The fraction of $N_2^+ (X, v > 0)$ was typically 30 to 40% of the total N_2^+ ion signal. The energy dependences of the two rate coefficients $k_{r,v=0}$ and $k_{r,v\neq 0}$ are presented in Fig. 3 together with the respective rate coefficients obtained very recently by Smith and Adams[20] in the Birmingham SIFT (selected ion flow tube)[27] at room temperature, the values being 1.7×10^{-13} cm^3 sec^{-1} and 4×10^{-10} cm^3 sec^{-1}, respectively.[20] Despite the big difference of more than three orders of magnitude, in the values of $k_{r,v\neq 0}$ and $k_{r,v=0'}$, both rate coefficients rapidly converge at $E_{c.m.}$ of a few eV due to the enormously strong increase of $k_{r,v=0}$ with $E_{c.m.}$.

The reaction

$$N_2^+ + Ar \rightarrow Ar^+ (^2P_{3/2}) + N_2 \tag{6}$$

is endothermic by 0.183 eV for N_2^+ ions in the $v = 0$ state and exothermic for $v \neq 0$. Thus one would expect an upper limit for the observed room-temperature value of $k_{r,v=0}$ to be

$$k_{\text{expected}} \leq k_L \exp[-(\Delta E/kT)], \tag{7}$$

with ΔE being the endothermicity of the reaction and k_L the Langevin limiting value[28] for the reaction. With $\exp[-(\Delta E/kT)]$ being about 10^{-3} in the present case and $k_L \sim 7\times 10^{-10}$ cm^3 sec^{-1}, we get $k_{\text{expected}} \leq 5\times 10^{-13}$, which is quite close to the observed thermal value of 1.7×10^{-13} cm^3 sec^{-1}. Thus, the lower set of rate coefficients in Fig. 3 indeed seems to represent $k_{r,v=0}$ for the reaction

$$N_2^+ (X, v = 0) + Ar \xrightarrow{k_{r,v=0}} Ar^+ (^2P_{3/2}) + N_2 (X, v = 0). \tag{8}$$

The following reasons lead us to believe that the larger rate coefficients in Fig. 3 may be attributed to the reaction

$$N_2^+ (X, v \neq 0) + Ar \xrightarrow{k_{r,v>0}} Ar^+ (^2P_{3/2}) + N_2. \tag{9}$$

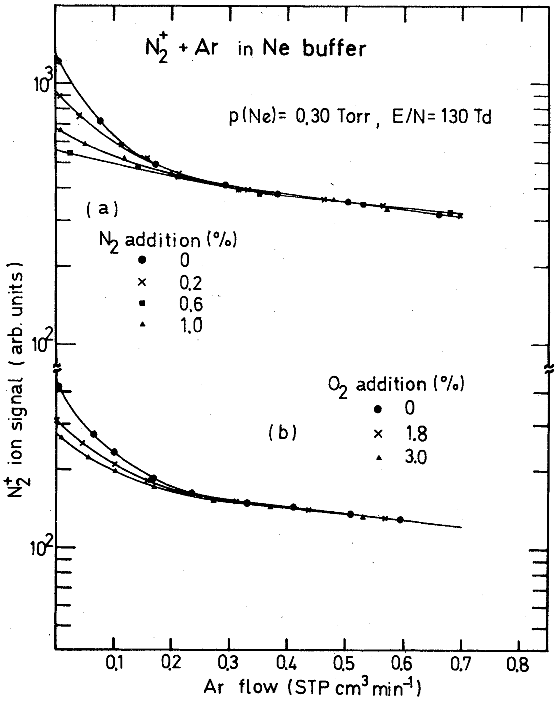

FIG. 4. N_2^+ ion signals as a function of the Ar reactant flow are shown (a) with various additions of N_2, and (b) of O_2 to the buffer. The fast reacting N_2^+ fraction $[N_2^+ (X, v > 0)]$ is removed much faster by N_2 than by O_2. The various sets of data are normalized at an Ar flow of 0.4 STP cm^3 min^{-1}.

(1). Addition of N_2 to the buffer gas leads to a fast decrease in the percentage of the "fast reacting N_2^+ fraction," as is shown in Fig. 4, most likely due to the quenching reaction

$$N_2^+ (X, v > 0) + N_2 \xrightarrow{k_q} N_2^+ (X, v = 0) + N_2, \tag{10}$$

whereas addition of O_2 to the buffer gas causes much less quenching. It is quite typical for vibrationally excited molecular ions to be quenched to the $v = 0$ level at a fast rate [near the Langevin or average dipole orientation (ADO) limiting value] by charge transfer with the parent gas, as was shown also for vibrationally excited O_2^+ and CO_2^+ ions.[29] An estimation of k_q from the data in Fig. 4 leads to a value of about 4×10^{-10} cm^3 sec^{-1} $\pm^{100}_{50}$%, whereas the quenching of $N_2^+ (X, v > 0)$ by O_2 is nearly an order of magnitude less effective.

(2) A check performed in the Birmingham SIFT[20] as well as in the present investigation using an electron impact ion source, showed the fraction of excited N_2^+ to stay nearly constant, even when the electron energy was decreased to values just slightly above the ionization threshold of N_2, so that higher electronic states of N_2^+ can be ruled out. While rotational excitation is cooled by only

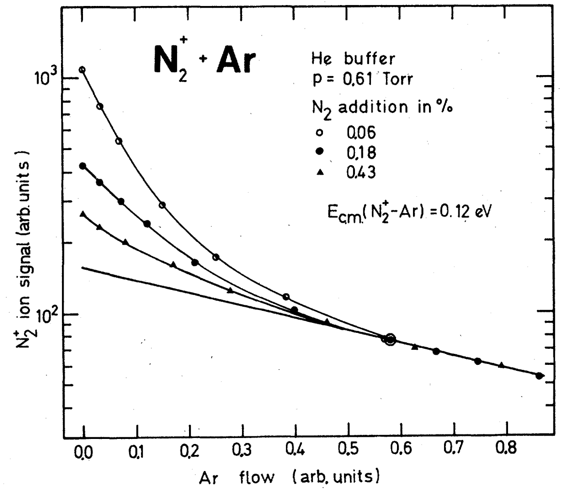

FIG. 5. Declines of the N_2^+ ion signals as a function of the Ar reactant gas flow. In all these cases the N_2^+ ions were produced via reaction $Ar^+ + N_2 \rightarrow N_2^+ + Ar$ by injecting Ar^+ to the helium-buffered drift region and adding traces of N_2 to the buffer. The data sets are normalized to the point indicated by ⊙.

a few collisions, vibrational excitation survives typically 10^4 collisions in a helium buffer,[29] which again suggests the fast reacting N_2^+ to be in vibrationally excited states.

C. More details on the forward reaction $Ar^+ + N_2 \xrightarrow{k_f} N_2^+ + Ar$

Despite the apparent exothermicity of this reaction, its room-temperature value of 1×10^{-11} cm^3 sec^{-1} lies by a factor of about 100 below the respective Langevin limiting value $k_L = 7 \times 10^{-10}$ cm^3 sec^{-1}. In fact, the following check showed this reaction not predominantly to go into the exothermic channel

$$Ar^+ ({}^2P_{3/2}) + N_2 \rightarrow N_2^+ (X, v=0) + Ar\,, \qquad (11)$$

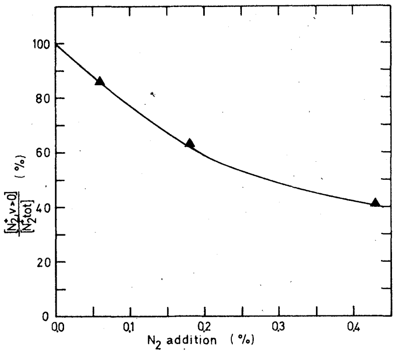

FIG. 6. Fraction of vibrationally excited N_2^+ to the total N_2^+ density as a function of N_2 addition to the buffer gas, as derived from Fig. 5.

but somewhat surprisingly rather into the channel

$$Ar^+ ({}^2P_{3/2}) + N_2 \xrightarrow{k_f} N_2^+ (X, v=1) + Ar\,, \qquad (12)$$

which is endoergic by 0.09 eV.

Ar^+ ions, generated in an electron impact ion source were injected into the drift section, where small amounts of N_2 were added to allow for reaction (1) under conditions where $E_{c.m.}$ was 0.12 eV and (see Fig. 5) where k_f was at about 4.5×10^{-11} cm^3 sec^{-1}. The addition of N_2 was kept constant at various values and was low enough, so that only some 10 to 20% Ar^+ were converted into N_2^+. Continuous addition of Ar as a reactant to the He buffer now led to two declines of the N_2^+ signal, the fast decline indicating that a high fraction of the N_2^+ ions were in the N_2^+ $(X, v=1)$ state. The smaller the amount of N_2 present in the buffer, the higher was the fraction of N_2^+ $(X, v=1)$ observed, in one case as high as 86%. Most likely all the N_2^+ in the $v=0$ state present in this check stems from N_2^+ $(X, v>0)$ which was quenched in the fast reaction (10), so that reaction (5) may lead to the product N_2^+ $(X, v>0)$ with a high probability of nearly 100%. An extrapolation of the fraction $[N_2^+ (v>0)]/[N_2^+{}_{tot}]$ from the data in Fig. 5 to zero N_2 addition to the buffer is in fact leading to a value of about 100% as shown in Fig. 6.

Under the assumption that channel (12) was the main path for reaction (1), the endoergicity of 0.09 eV would lead using relation (7) with $k_L = 7 \times 10^{-10}$ cm^3 sec^{-1} in this case to an upper limit for k_f at room temperature of 2×10^{-11} cm^3 sec^{-1}, which is indeed just slightly above the observed value of 1×10^{-11} cm^3 sec^{-1}. Smith and Adams[20] find that, at room temperature, channel (12) leading to N_2^+ $(X, v=1)$ makes up for about 60–70% of the total reaction, whereas at 80 K only $N_2^+ (X, v=0)$ is produced. Thus there is a drastic change in the reaction channels as a function of temperature or energy. Channel (11), leading to N_2^+ $(X, v=0)$ decreases with increasing temperature, while the endoergic channel (12) into N_2^+ $(X, v>0)$ increases strongly in accordance with thermodynamic expectations. The sum of both channels thus leads to the minimum of k_f at 140 K as observed by Smith and Adams.[20]

D. Data on k_r obtained from equilibrium constants in Ar-N_2 mixtures

Earlier investigations on the energy dependences of the proton-transfer reactions

$$N_2OH^+ + CO \rightleftharpoons COH^+ + N_2O\,, \qquad (13)$$

performed in the NOAA-flow drift tube[30] showed marked differences between the rate coefficients obtained in a helium and an argon buffer, respec-

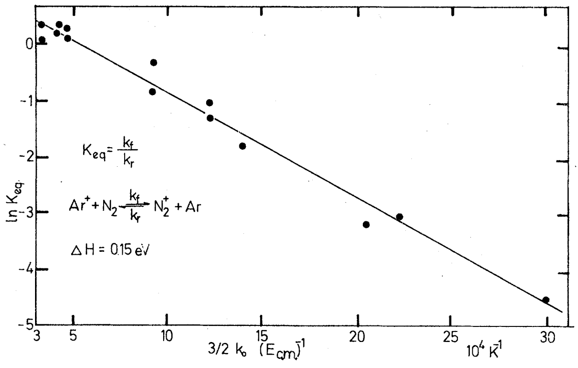

FIG. 7. Van't Hoff plot for the reaction $Ar^+ + N_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2^+ + Ar$. The equilibrium constants were taken in an argon buffer at various E/N values. $E_{c.m.}$ denotes the mean relative kinetic energy between Ar^+ and N_2, calculated in the usual way (Ref. 5).

tively. A comparison with data taken in a temperature variable flowing afterglow showed the set of temperature data to lie close to the argon buffer data (see Fig. 2 in Ref. 30), while the set of data obtained in a helium buffer was markedly shifted away from both the temperature and argon buffer data.

This can be understood by the generally higher efficiency for vibrational excitation of molecular ions drifting in argon compared to helium. From these results and similar other ones one may conclude that drift data obtained in an argon buffer do resemble temperature data to some degree of accuracy. We therefore obtained the equilibrium constants K at various E/N values,

$$K = \frac{k_f}{k_r} = \frac{[N_2^+][Ar]}{[Ar^+][N_2]} \tag{14}$$

in the usual way (Fig. 2 of Ref. 33). These data were used to draw a Van't Hoff plot (Fig. 7) to estimate the effective enthalpy change for the charge-transfer reaction (1). In order to attribute any meaning to a Van't Hoff plot, taken from drift equilibrium data, it is necessary that at the various E/N values the relative kinetic energies $E_{c.m.}$ between N_2^+ and Ar be very similar to those of Ar^+ and N_2. Owing to fortuitous mobility values of Ar^+ and N_2^+ in Ar this condition is met to some extent. The enthalpy difference, ΔH deduced from Fig. 7 is 0.15 eV, which comes quite close to the energy difference of 0.183 eV between the lowest states of Ar^+ and of N_2^+. In a further step we calculated the reverse rate coefficients $k_{r\,\mathrm{temp}}$ from the equilibrium constants K and the rate coefficients k_f of the forward reaction,

$$k_{r,\mathrm{temp}} = k_f / K \,, \tag{15}$$

the results being shown in Fig. 8. There is excellent agreement between the present values near room temperature and the ones obtained by Smith and Adams,[20] and also the much steeper increase of $k_{r,\mathrm{temp}}$ with respect to $k_{r,v=0}$ occurs as expected, because $k_{r,\mathrm{temp}}$ should resemble quite closely the reverse rate coefficient as dependent on true temperature. As has been shown in Sec. III B, vibrational excitation enhances the reverse rate coefficient dramatically, thus $k_{r,\mathrm{temp}}$ has to be considerably higher than $k_{r,v=0}$ at elevated energies, again similar to the case of the proton-transfer reaction (13) mentioned above.

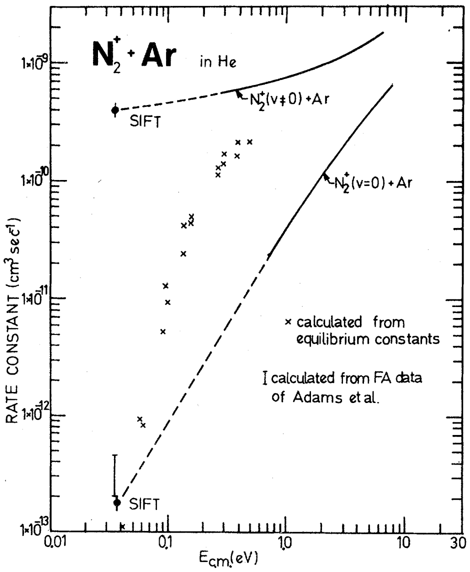

FIG. 8. Energy dependence of the rate coefficient $k_{r,\mathrm{temp}}$ of the reverse reaction $N_2^+ + Ar \rightarrow Ar^+ + N_2$ as calculated from equilibrium constants obtained in an argon buffer (x). Also shown for comparison are data from Fig. 3, and of Smith and Adams[20] as well as limits for $k_{r,\mathrm{temp}}$ estimated from data of Adams *et al.*,[16] as described in Sec. III D.

E. Discussion of earlier results

With the above results on the reverse reaction (2) it is obvious that rate coefficients for the reaction of Ar^+ with N_2 measured in an argon buffer or in He-Ar mixtures are falsified by the back reaction (2) and thus the observed effective rate coefficients are too low with respect to the true value k_f, which is 1×10^{-11} $cm^3 sec^{-1}$ at room temperature. Thus the low values reported from various flowing afterglows[15,16,19] and from a stationary afterglow[14] experiment all listed in Table I, are not surprising. From the above-mentioned results of Adams *et al.*,[16] who measured k_f as dependent on the argon addition to the helium buffer in a flowing afterglow, it is even possible to get a quantitative estimation on the value for the reverse reaction (2).

Disregarding other effects, discussed later, the balance of the Ar^+ ion density $[\mathrm{Ar}^+]$ is given by

$$\frac{d[\mathrm{Ar}^+]}{dt} = -k_f[\mathrm{Ar}^+][\mathrm{N}_2] + k_r[\mathrm{N}_2^+][\mathrm{Ar}]\,. \qquad (16)$$

As the loss of an Ar^+ ion always results in the gain of a N_2^+ ion and vice versa, we conclude

$$\frac{d[\mathrm{N}_2^+]}{dt} = -\frac{d[\mathrm{Ar}^+]}{dt}\,. \qquad (17)$$

In a flow system, such as the flowing afterglow, the reaction time t is correlated to the reaction distance x by x/v, with v being the flow velocity of the buffer gas.

Integration of (17) results in

$$[\mathrm{N}_2^+] + [\mathrm{Ar}^+] = \mathrm{const} = [\mathrm{Ar}^+]_0\,, \qquad (18)$$

and substitution into (16) leads to

$$\frac{d[\mathrm{Ar}^+]}{dx} = \left(-\frac{k_f}{v}[\mathrm{N}_2] - \frac{k_r}{v}[\mathrm{Ar}]\right)[\mathrm{Ar}^+] + \frac{k_r}{v}[\mathrm{Ar}][\mathrm{Ar}^+]_0\,. \qquad (19)$$

By integration we get

$$[\mathrm{Ar}^+] = C\exp\left(-\frac{k_f}{v}[\mathrm{N}_2] - \frac{k_r}{v}[\mathrm{Ar}]\right)x + \frac{k_r[\mathrm{Ar}][\mathrm{Ar}^+]_0}{k_f[\mathrm{N}_2] + k_r[\mathrm{Ar}]}\,. \qquad (20)$$

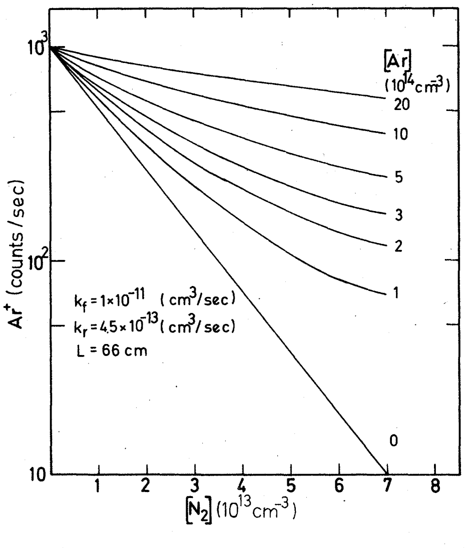

FIG. 9. Ar^+ signal as a function of the density of N_2 added to the helium buffer, calculated according to Eq. (22). The density of Ar also present in the buffer was varied from 0 to 20×10^{14} cm^{-3}.

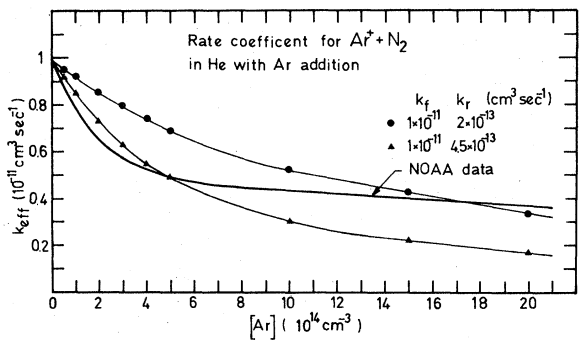

FIG. 10. Effective rate coefficients as calculated from the initial Ar^+ signal declines of the type shown in Fig. 9. Measured effective rate coefficients are shown for comparison of Adams *et al.* (Ref. 16).

In any case at $x = 0$ the concentration $[\mathrm{Ar}^+]_{x=0}$ equals $[\mathrm{Ar}^+]_0$, thus the integration constant C has to be

$$C = [\mathrm{Ar}^+]_0\left(1 - \frac{k_r[\mathrm{Ar}]}{k_f[\mathrm{N}_2] + k_r[\mathrm{Ar}]}\right), \qquad (21)$$

and the Ar^+ density as a function of the reaction length therefore is given by

$$[\mathrm{Ar}^+] = [\mathrm{Ar}^+]_0\left(1 - \frac{k_r[\mathrm{Ar}]}{k_f[\mathrm{N}_2] + k_r[\mathrm{Ar}]}\right) \times\exp\left(-\frac{x}{v}(k_f[\mathrm{N}_2] + k_r[\mathrm{Ar}])\right) + \frac{k_r[\mathrm{Ar}]}{k_f[\mathrm{N}_2] + k_r[\mathrm{Ar}]}[\mathrm{Ar}^+]_0\,. \qquad (22)$$

Using this equation, the relative declines of Ar^+ densities are calculated as dependent on the N_2 reactant-gas addition to the buffer gas (helium). The parameter is the argon concentration in the buffer, and the reaction rate coefficients for the forward and reverse reactions are assumed to be 1×10^{-11} cm^{3}sec^{-1} and 4.5×10^{-13} cm^{3}sec^{-1}, respectively.

The reaction length of 66 cm and flow velocity of 10^4 cm/sec are assumed to be close to the actual values present in the experiment of Adams *et al.*[16] The set of "effective" rate coefficients calculated from the initial declines in Fig. 9 are plotted in Fig. 10 together with a second set calculated under the assumption that k_r be 2×10^{-13} cm^{3}sec^{-1}. For comparison, the measured "effective" rate coefficients of Adams *et al.*[16] are shown.

A comparison of the measured and calculated data shows a better than qualitative agreement, from which the true value of k_r may well be concluded to lie somewhere in the range from two to a few times 10^{-13} cm^{3}sec^{-1}. This is a reasonable result, especially as the above estimate is oversimplified in that it does not take into account the fact that the product N_2^+ of reaction (1) is predominantly in the $v = 1$ state, which then may either react with Ar in the fast reaction (9) or be quenched to the $v = 0$ state in a collision with N_2 by reaction (10), before it may react according to (8) as indicated in the above formula (16). Also neglected in the above estimate is the influence on k_f by the difference in the diffusion coefficients of N_2^+ and Ar^+ in the helium buffer. Such an influence however should be very small, otherwise in the experimental data of Adams *et al.*,[16] a pressure dependence of k_f should have been observed, which was not the case. Taking all these uncertainties into account the result of the above calculation agrees very well with the present measurements and the one of Smith and Adams[20] (see Fig. 8).

IV. CONCLUSIONS

The present results seem to resolve the uncertainties in the literature on reaction (1) and infer that both the forward and the reverse reaction (1) and (2), respectively, proceed via channels which have to overcome energy barriers. Additional investigations on the question whether the $^2P_{1/2}$ state of Ar^+ reacts with the same rate coefficient with N_2 as the $^2P_{3/2}$ state or rather is quenched by N_2 to the $^2P_{3/2}$ state would be highly desirable.

Dr. D. Smith and Dr. F. C. Fehsenfeld kindly drew our attention to a recent paper by Rakshit and Warneck,[31] where a low value of $k_5 = 3.7 \times 10^{-12}$ $cm^3\ sec^{-1}$ for the rate coefficient of reaction (5) obtained in a drift experiment was reported. As in some other cases discussed above, Rakshit and Warneck used argon as a buffer, but did not account for the back reaction (6), thus obtaining too small rate coefficients k_5. A detailed comment on the paper by Rakshit and Warneck will be published elsewhere.[32]

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