

Behavior of rate coefficients for ion-ion mutual neutralization, 300–550 K

Thomas M. Miller, Nicholas S. Shuman, and A. A. Viggiano

Citation: *The Journal of Chemical Physics* **136**, 204306 (2012); doi: 10.1063/1.4720499

View online: <https://doi.org/10.1063/1.4720499>

View Table of Contents: <http://aip.scitation.org/toc/jcp/136/20>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[Kinetics of ion-ion mutual neutralization: Halide anions with polyatomic cations](#)

The Journal of Chemical Physics **140**, 224309 (2014); 10.1063/1.4879780

[Temperature dependences for the reactions of \$O_2^-\$ and \$O^-\$ with N and O atoms in a selected-ion flow tube instrument](#)

The Journal of Chemical Physics **139**, 144302 (2013); 10.1063/1.4824018

[Flowing afterglow measurements of the density dependence of gas-phase ion-ion mutual neutralization reactions](#)

The Journal of Chemical Physics **138**, 204302 (2013); 10.1063/1.4803159

[Kinetics of electron attachment to OH and \$HNO_3\$ and mutual neutralization of \$Ar^+\$ with \$NO_2^-\$ and \$NO_3^-\$ at 300 and 500 K](#)

The Journal of Chemical Physics **136**, 124307 (2012); 10.1063/1.3694876

[Electron attachment to \$POCl_3\$. III. Measurement and kinetic modeling of branching fractions](#)

The Journal of Chemical Physics **134**, 094310 (2011); 10.1063/1.3549139

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY



Behavior of rate coefficients for ion-ion mutual neutralization, 300–550 K

Thomas M. Miller,^{a)} Nicholas S. Shuman, and A. A. Viggiano

Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base,
New Mexico 87117-5776, USA

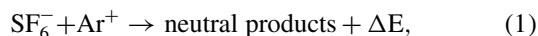
(Received 10 February 2012; accepted 7 May 2012; published online 24 May 2012)

Rate coefficients k_{MN} have been measured for a number of anion neutralization reactions with Ar^+ and Kr^+ over the temperature range 300–550 K. For the first time, the data set includes anions of radicals and other short-lived species. In the present paper, we review these results and make note of correlations with reduced mass, electron binding energy of the anion (equivalent to the electron affinity of the corresponding neutral), and temperature, and compare with expectations from absorbing sphere models. An intriguing result is that the data for diatomic anions neutralized by Ar^+ and Kr^+ have k_{MN} values close to $3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, a figure which is lower than those for all of the polyatomic anions at 300 K except for $\text{SF}_5^- + \text{Kr}^+$. For the polyatomic anions studied here, neutralized by Ar^+ and Kr^+ , the reduced mass dependence agrees with theory, on average, but we find a stronger temperature dependence of $T^{-0.9}$ than expected from the theoretical $E^{-0.5}$ energy dependence of the rate coefficient at thermal energies. The k_{MN} show a weak dependence on the electron binding energy of the anion for the polyatomic species studied. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4720499>]

I. INTRODUCTION

Mutual neutralization (MN) of anion-cation pairs is the process that limits plasma density in situations where few free electrons exist, such as in flames, electronegative discharges, gas laser media, and in the lower atmosphere (including the D-region of the ionosphere at night). Because of the strong, long-range Coulomb potential, MN of molecular ions is characterized by large cross sections, as much as $10\,000 \text{ Å}^2$, at low energies. In most cases, the reaction is highly exothermic, so the product may be electronically excited or dissociated. A brief history of the MN problem was given in an earlier paper,¹ starting with recognition of the process and the first measurement of a rate coefficient, by J. J. Thomson and Ernest Rutherford in 1896.² However, according to a more extensive history by Loeb, valid measurements only came about after World War II due to new developments with mass spectrometry, photomultiplier tubes, fast oscilloscopes, and microwave discharge techniques.³ Mutual neutralization can take place either as a binary or a ternary process with a neutral third body. Early experimental work concerned gas pressures for which the ternary process dominated.³ In ternary MN, the effective binary rate coefficient is seen to rise with pressure until the point that the buffer gas begins to interfere with the MN process (in the neighborhood of 1000 Torr in air) instead of assisting it, because of decreased ion mobility in the electric field between the interacting ion pair.^{4,5} Thus, the rate coefficient decreases with higher pressure.

The present paper is concerned with binary MN, e.g.,



in which an electron is transferred from the anion to the cation via avoided crossings between the incoming Coulomb poten-

tial surface and one or several neutral potential exit channels. The exothermicity, ΔE , ends up as excitation energy, kinetic energy of the products, and bond scission energy.

In principle, an exact calculation of the cross section for the MN process is possible: one calculates the potential surfaces for all states of the reaction and uses coupled-channel methods to calculate transition probabilities for the avoided crossings, from which the cross sections follow. Only for the reaction $\text{H}^- + \text{H}^+$ is this procedure tractable.⁶ A more economical approach is based on the Landau-Zener method, but some approximation must be made for the coupling matrix elements at curve-crossing points, which limits the accuracy to a factor of 3 at best.⁷ For molecular ions, the number of avoided crossings is so large that Olson developed an “absorbing sphere” model in which neutralization occurs with unit probability if the ion pair approaches within a critical separation distance.⁷ The critical distance R_c was calculated using Landau-Zener theory and semi-empirical coupling matrix elements. The absorbing sphere model requires only two inputs: the reduced mass (μ) and the electron binding energy of the anion (E_a), the latter equivalent to the electron affinity of the corresponding neutral if the anion is in its ground state. In addition to E_a , the electron acceptance energy of the cation determines the steepness of the ionic curve and hence is implicitly contained within R_c . R_c is found to depend most strongly on E_a and only logarithmically on μ .⁸ The critical distances commonly lie between 8 and 25 Å.⁷ At larger distances, the coupling matrix elements die off exponentially. At shorter distances, the particles on the ionic surface have high velocities, which makes transition to a neutral surface unlikely and in any case, the small impact parameter contributes little to the overall MN cross section. Hickman later developed a generalization of the absorbing sphere model with a complex potential which provided for crossings over a neighborhood around R_c , in effect smoothing the crossing point.⁸ Hickman

^{a)} Also at Institute for Scientific Research, Boston College, Chestnut Hill, Massachusetts 02467, USA.

carried out numerical calculations of rate coefficients for MN (k_{MN}) for a variety of cases (with E_a ranging from that for H^- to that for Cl^-) and found that $k_{\text{MN}} \times \mu^{0.5}$ was approximately dependent on $E_a^{-0.4}$, and presented a parameterized formula for k_{MN} in terms of temperature (T), reduced mass of the ionic pair (μ), and electron binding energy for the anion (E_a)

$$k_{\text{MN}} = 5.35 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} (T/300)^{-0.5} \mu^{-0.5} E_a^{-0.4},$$

$$T \leq 1000 \text{ K}, \quad (2)$$

where k_{MN} is in $\text{cm}^3 \text{ s}^{-1}$ for T in K, μ in atomic mass units, and E_a in eV. Hickman's fit to merged beams data available at the time (obtained with relative collision energies ≥ 0.15 eV) showed that experimental data tended to lie lower in k_{MN} value than predicted by Eq. (2), but not always, and generally better than the absorbing sphere model. Fitting Eq. (2) to MN data from flowing afterglow experiments (obtained under truly thermal conditions; Refs. 9–14) supported the parameterizations, though with a weaker dependence on E_a (an exponent of -0.24 or lower) and a smaller prefactor ($3.32 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$).¹⁵ Because the k_{MN} for molecular ions do not vary much, any such parameterization fit to experimental data – even a fixed value – will yield results no more than 40% off. It is worth noting fundamental assumptions in the absorbing sphere model. According to Hickman, the initial Coulombic trajectory, embedded in the continuum, is assumed to cross neutral states so closely spaced that transitions may be considered to occur continuously along the trajectory, rather than at isolated curve crossings, and the probability of transitions from the neutral channels back to the ionic channel must be negligible. Further, ground state ions are assumed.

A similar approach was taken by Bopp *et al.*, but using a different semi-empirical estimate for the interaction energy at the crossing point developed for alkali halide systems, and allowing for double crossing and Franck-Condon overlap.¹⁶ The method led to smaller R_c than found in the absorbing sphere model discussed above, and hence smaller k_{MN} , primarily due to a probability factor of 0.5 modifying the expression for k_{MN} to account for double passage. The end result is values of k_{MN} a factor of 3 below those of Olson, placing the k_{MN} of Bopp *et al.* in better agreement (5%–35%) with the present data for the systems considered in Ref. 15 (SF_6^- , SF_5^- , and SF_4^- neutralized by Ar^+).

In recent years, we have developed a method called variable electron and neutral density attachment mass spectrometry (VENDAMS) which utilizes a flowing-afterglow Langmuir-probe (FALP) apparatus in a new way.¹⁷ The power of the VENDAMS method is that we can study electron attachment to fragments of molecules (radicals and other short-lived species) formed in dissociative electron attachment with stable species. We can then study the neutralization of the anions formed from molecular fragments in collision with noble gas cations, which has not been done previously. Anions formed from radicals tend to be singlets, in contrast to the doublet anions studied in past MN research. Additionally in VENDAMS, k_{MN} are determined without measuring ion densities using the Langmuir probe, obviating the need

for further corrections.¹⁸ In the present paper, we pull together all of the VENDAMS MN measurements and note correlations.

II. EXPERIMENT

The VENDAMS method¹⁷ utilizes a conventional FALP apparatus.^{19–21} In our FALP, a fast flow of He buffer gas (17 standard liters per minute) is passed down the length of a tube (7-cm diameter, 1-m long) at typically $3.2 \times 10^{16} \text{ cm}^{-3}$ at all temperatures (1 Torr at 300 K). Reactions taking place along the length of the flow tube may be observed and rate coefficients derived, using the plasma velocity of the flow (100 m s^{-1}) to provide the time scale. The He gas is cleansed of condensibles in a liquid-nitrogen trap, warmed, then passed through a microwave discharge cavity to provide a plasma. A small flow of Ar or Kr gas (2%–4%) is added downstream of the discharge to remove metastable He^* by Penning ionization of the noble gas and to remove He_2^+ ions by charge transfer. The result is an electron- Ar^+ or Kr^+ plasma (with $\sim 5\%$ He^+ at 300 K), passing down the flow tube. At a point approximately halfway down the flow tube, a reactant gas is admitted through an inlet that consists of 4 hollow, radial needles, with the purpose of distributing the reactant gas as uniformly as possible across a cross section of the flow tube. Plasma density along the flow tube is lost by ambipolar diffusion. If the reactant gas molecules attach electrons, the plasma density decays even faster downstream of the inlet. The electron density may be measured along the flow tube axis using a movable Langmuir probe.²² The Langmuir probe is used to measure the plasma velocity (via a small pulse on the discharge), the ambipolar diffusion rate, and the faster decay due to electron attachment. An electron attachment rate coefficient may be determined by fitting the observed electron density data, accounting for both the diffusion and attachment reactions.^{19–21} Mass spectrometric sampling of the plasma at the terminus of the flow tube provides information on the anion products of the attachment reaction. Under various conditions, FALP apparatuses have been used to measure rate coefficients for electron attachment,^{19,21} electron-ion recombination,^{23,24} electron temperature relaxation,²⁵ diffusion cooling,²⁶ ion-molecule reaction,²⁷ and anion-cation MN.^{9–14}

Accurate electron density (denoted by $[e]$) measurements require satisfying certain conditions for a cylindrical Langmuir probe.²² The plasma sheath radius should be greater than the radius ($13 \mu\text{m}$ in this case) of the probe wire but much less than the probe length (7 mm in this case). The sheath radius is calculated to be $940 \mu\text{m}$ at $[e] = 10^9 \text{ cm}^{-3}$ and $94 \mu\text{m}$ at 10^{11} cm^{-3} for a 1-V potential. Electrons should not make any collisions with gas in spiraling toward the probe within the sheath, a condition satisfied at our He pressure.²² The Langmuir probe measurement of $[e]$ is usually considered accurate to $\pm 10\%$ for $[e]$ in the range 10^9 – 10^{11} cm^{-3} , limited primarily in knowing exactly the current-collecting surface area of the probe.^{19,22} As a test, we have made measurements of electron- O_2^+ recombination at 300 K in this density range and agreed to 9% with the accepted rate coefficient (of just under $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$).¹⁹

In the VENDAMS method, the Langmuir probe is used to measure the electron density at the position of the reactant inlet, i.e., $t = 0$, but is not used to follow the electron density decay downstream of the inlet as in the conventional FALP measurements. Instead, the anion signals from the mass spectrometer are recorded as the initial electron density, $[e]_0$, is increased, starting at a low value ($<10^9 \text{ cm}^{-3}$) where only diffusion and electron attachment take place, up to large values ($5 \times 10^{10} \text{ cm}^{-3}$) where secondary and tertiary processes occur. These data allow us to model the plasma processes and determine rate coefficients for the secondary and tertiary processes. The most important consequences have been (a) obtaining information on the fragmentation of anions in the MN process, (b) the determination of rate coefficients for electron attachment and MN for radicals or other short-lived species in the afterglow, and (c) identification of a new process, electron-catalyzed MN.^{28,29} The details of these determinations are left to individual papers cited below, which describe the VENDAMS method and analysis of data, including the procedure for assigning uncertainties. The present paper focuses on the binary k_{MN} measured thus far. Information on the fragmentation of anions undergoing MN will not be discussed in this paper.

Briefly, VENDAMS measurements for MN involves adding two neutral precursor gases through a single inlet to the established noble gas cation/ e^- plasma. One of the precursors undergoes dissociative electron attachment to yield a monatomic anion, e.g., Cl^- or Br^- , and the other undergoes electron attachment to yield the polyatomic anion of interest. Typical neutral concentrations are $\sim 2 \times 10^9 \text{ cm}^{-3}$ for the polyatomic anion precursor and $\sim 2 \times 10^{10} \text{ cm}^{-3}$ for the monatomic anion precursor. Typically, the latter is a fast attaching species (such as CCl_4 or CF_2Br_2) and the larger concentration serves a second purpose of quickly depleting the electron density within a few cm of the reactant inlet; without electrons present secondary attachment is inhibited and the anion abundances evolve in time only through MN and ambipolar diffusion. By setting up the conditions optimally, there is only one unknown in the data reduction. Alternatively, if an attaching gas produces both an atomic and polyatomic anion upon electron attachment (e.g., Cl^- and PSCl_2^- from PSCl_3), then a single gas is satisfactory.

The key to success of the two-gas method for measuring k_{MN} is the observation that monatomic anion-cation pairs generally undergo MN with a k_{MN} at least one order of magnitude lower than if either is polyatomic (or diatomic). While there are exceptions to this rule (e.g., $\text{H}^+ + \text{H}^-$), we have not found such an exception for the systems we have studied (Ar^+ or Kr^+ with Cl^- or Br^-). The simultaneous presence of a monatomic anion and a polyatomic anion thus allows a direct comparison of rate coefficients to be made. At low $[e]_0$ ($\leq 10^9 \text{ cm}^{-3}$), the primary electron attachments occur, but the concentration of ions is too low for MN to occur at an appreciable rate, and the relative anion abundances reflect the relative concentrations and attachment rate coefficients of the neutral precursors. At higher $[e]_0$ ($\gtrsim 5 \times 10^9 \text{ cm}^{-3}$), the polyatomic anion undergoes MN with Ar^+ (or Kr^+) at an increasingly faster rate while the monatomic ions still neutralize at a negligible rate. The observed decrease in the poly-

atomic anion abundance with increasing $[e]_0$ is modeled as described in Ref. 17 in order to extract k_{MN} . We fit the data to a model and a Monte Carlo procedure described in Ref. 17 which yields k_{MN} and the uncertainty. Under typical conditions, the uncertainty has been found to be $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, regardless of the magnitude of the rate coefficient. A potential error in the k_{MN} is due to the $\sim 5\%$ He^+ that remains in the plasma. The absorbing sphere model indicates that neutralization by He^+ should be about 1.7 times greater than by Ar^+ . This translates into an 8% error in the derivation, which is included in our error limit.

The VENDAMS method limits us to MN reactions only with noble gas atomic cations. On one hand, limitation to noble gas atomic cations seems severe, but on the other, the range of molecular anion reactants available is immense and will provide a database which may be more theoretically tractable than if both species are molecular, particularly since the theoretical treatments discussed above depend only on the electron binding energy of the anion and not directly on the electron capture energy of the cation.

The VENDAMS MN measurements are thus complementary to the earlier FALP MN measurements. The earlier measurements⁹⁻¹⁴ utilized a large concentration of reactant gas to convert an electron- He^* , He^+ afterglow plasma to an anion-cation plasma in as short a distance following the inlet as possible (1–2 cm), and the Langmuir probe was used to measure the ion densities. Thus, while a large range of molecular cations were studied in the earlier work, it was not possible to study MN reactions with a noble gas atomic cation because reactions with He^* and He^+ took place quickly. Mutual neutralization reactions with atomic anions, e.g., Cl^- , were studied, and by clever tricks, Church and Smith were able to set upper limits on k_{MN} for the MN reactions $\text{Ar}^+ + \text{F}^-$, $\text{Kr}^+ + \text{F}^-$, $\text{Xe}^+ + \text{F}^-$, and $\text{Xe}^+ + \text{Cl}^-$, which are important for VENDAMS work.¹² Strictly speaking, the VENDAMS method measures the difference between anion-cation and those for atomic anion-atomic cation reaction. VENDAMS studies of neutralization of Ar^+ with F^- , Cl^- , and Br^- show that k_{MN} of those reactions differ by less than the uncertainty of the experiments. Those atomic reactions are assumed to occur at least 10 times slower than the molecular MN reaction studied with VENDAMS and therefore errors related to this assumption are deemed well within our uncertainty.

III. RESULTS AND CORRELATIONS

Mutual neutralization rate coefficients measured thus far with the VENDAMS method are listed in Table I, consisting of data reported in Refs. 17, and 28–39 and including some new MN data not yet published. Because the electron binding energy of the anion is deemed an important parameter, at least in theory, the electron affinity (E_a) of the corresponding neutral molecule is also listed, along with the critical curve-crossing radius R_c (Ref. 7). Figure 1 shows a comparison of the present data with Landau-Zener theory: the absorbing sphere model of Olson,⁷ the complex potential generalization of Hickman,⁸ and calculations of Bopp *et al.*¹⁶ for SF_4^- , SF_5^- , and SF_6^- neutralized by Ar^+ , using a different curve crossing interaction energy and allowing for double passage

TABLE I. Mutual neutralization rate coefficients k_{MN} measured using the VENDAMS method. Experimental uncertainties in the final digit(s) are given in parentheses. E_a is the electron binding energy in the anion (electron affinity of the corresponding neutral), μ is the reduced mass, and R_c is the critical curve crossing radius.⁷ Experimental E_a values were taken from Ref. 36 except for those of SF_6 (Ref. 39) and C_7F_{14} .³⁵ If a value of E_a is given without an uncertainty in parentheses, it means that the value was calculated using the G3 compound model of Curtiss *et al.*³⁷

Anion	Cation	k_{MN} in units of $10^{-8} \text{ cm}^3 \text{ s}^{-1}$				E_a (eV)	μ (amu)	R_c (Bohr)	References
		300 K	400 K	500 K	550 K				
Br_2^-	Ar^+	2.6(5)	1.8(5)	1.5(5)	...	2.55(10)	31.959	20.137	^a
Br_2^-	Kr^+	3.1(5)	2.3(5)	2.55(10)	54.974	20.359	^a
Cl_2^-	Ar^+	3.0(6)	2.4(5)	...	1.8(5)	2.38(10)	25.552	20.468	30
CN^-	Ar^+	3(1)	3.862(4)	15.750	16.598	31
FCI^-	Ar^+	3.0(8)	2.4(6)	1.5(4)	...	2.25(10) ^b	23.043	20.810	32
NO_2^-	Ar^+	5.2(20)	...	3.7(12)	...	2.273(5)	21.382	20.658	33
$PSCl^-$	Ar^+	5.4(11)	4.3(9)	...	3.9(10)	1.80	28.421	22.854	17
$COCl_2^-$	Ar^+	5.3(10)	4.3(9)	1.17	28.456	26.734	30
NO_3^-	Ar^+	4.5(25)	3.937(14)	24.295	16.788	33
$POCl_2^-$	Ar^+	4.6(7)	3.75(7)	3.0(6)	...	3.83(25)	29.837	17.124	29
$POCl_2^-$	Kr^+	3.6(5)	3.0(5)	1.8(5)	...	3.83(25)	48.980	17.487	^a
$PSCl_2^-$	Ar^+	4.5(7)	3.3(5)	...	2.6(5)	3.53	30.771	17.709	29
CF_3O^-	Ar^+	4.6(5)	3.2(5)	2.8(5)	2.3(5) ^c	4.56	27.177	16.139	^a
$POCl_3^-$	Ar^+	5.6(6)	4.5(6)	4.1(7)	...	1.41(20)	31.691	25.134	29
$POCl_3^-$	Kr^+	4.4(5)	3.5(5)	2.5(5)	...	1.41(20)	54.186	25.784	^a
SF_4^-	Ar^+	4.0(8)	3.3(8)	2.9(7)	...	1.5(2)	29.166	24.474	32
SF_4^-	Kr^+	3.6(5)	1.5(2)	47.199	25.041	^a
SF_5^-	Ar^+	3.5(5)	2.9(7)	2.6(7)	...	4.23(12)	30.393	16.473	32
SF_5^-	Kr^+	2.5(5)	4.23(12)	50.497	16.827	^a
SF_6^-	Ar^+	5.0(5)	3.7(6)	3.4(5)	...	1.03(5)	31.369	28.099	32
SF_6^-	Kr^+	3.7(5)	1.03(5)	53.250	28.415	^a
$Fe(CO)_4^-$	Ar^+	5.0(7)	2.36(10)	32.270	20.753	34
$c-C_6F_5^-$	Ar^+	5.5(13)	4.63	32.239	15.927	31
$C_7F_{14}^-$	Ar^+	4.8(5)	3.5(5)	3.1(5)	...	1.02(06)	35.856	28.386	35

^aUnpublished.

^bRecommended E_a from a computational study, Ref. 38; a few experimental values are quoted in Ref. 38.

^cThis one value was obtained at 600 K but is shown in the 550 K column for convenience.

and Franck-Condon factors. Power law fits to the calculated and measured k_{MN} are shown, but are expected to be only approximate matches to the results.

Figure 2 shows the temperature dependence of k_{MN} for those anions for which the temperature dependence was studied. The most striking feature of this figure is that the MN rate coefficients for diatomic anions reacting with Ar^+ or Kr^+ are all approximately $3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, a value which is uniformly lower than those for the polyatomic anion reactants at 300 K. While it may be risky to draw general conclusions from data for four diatomic anions, we note that the diatomic anions cover a wide range of μ (and a modest range in E_a ; a factor of 1.7) with little variation in k_{MN} , within uncertainties. The tentative conclusion is that the diatomic anions have too few electronic and vibrational levels crossing the Coulomb surface in the optimum R_c region for the absorbing sphere model to be applicable, for MN with Ar^+ and Kr^+ . Even so, one might expect that different Landau-Zener curve crossings would be active in Br_2^- , Cl_2^- , CN^- , and FCI^- in MN with Ar^+ and Kr^+ , so it is puzzling that the k_{MN} are rather invariant at any one temperature. The temperature dependence for the diatomic anions with Ar^+ and Kr^+ is $T^{-(1.1 \pm 0.2)}$, which is stronger than the theoretical $T^{-0.5}$ (see Fig. 2). In ear-

lier FALP work by Church and Smith, there is one case of a diatomic cation (Cl_2^+) neutralized by a monatomic anion (Cl^-), for which k_{MN} was found to be $5.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at $\sim 300 \text{ K}$.¹² More recent work on the same apparatus by Španěl and Smith yielded $k_{MN} = 2.0 \pm 0.5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ for NO^+ neutralized by either Cl^- or I^- at 300 K.⁴⁰

The polyatomic anions, including the two triatomic anions studied, show a broader range (though still rather narrow) of k_{MN} with Ar^+ at 300 K, from 3.5 to $5.6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$, somewhat lower than the earlier FALP data which showed a typical k_{MN} to be $6 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ for polyatomic ions and $7.5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ for ligated or cluster ions, on average.⁹⁻¹⁴ The average temperature dependence (Fig. 2) for polyatomic anions neutralized by Ar^+ and Kr^+ is $T^{-(0.9 \pm 0.1)}$. It should be noted that our uncertainty, typically $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, puts a greater fractional uncertainty on k_{MN} as the temperature increases (smaller k_{MN}), which limits the accuracy of the temperature exponent. As with the diatomic anions, this dependence is stronger than the $T^{-0.5}$ dependence predicted theoretically. This discrepancy, while not large given the experimental uncertainty, is worthy of further consideration because the $T^{-0.5}$ temperature dependence is a fundamental consequence of the Coulomb potential which

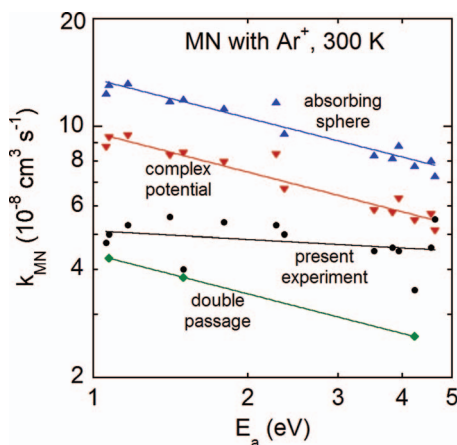


FIG. 1. A comparison of the present experimental mutual neutralization rate coefficients for polyatomic anions reacting with Ar^+ at 300 K (black circles), with the predictions of the absorbing sphere theory of Olson (blue upright triangles, Ref. 7), the complex potential extension of that theory by Hickman (red inverted triangles, Ref. 8), and the modification by Bopp *et al.* (green diamonds, Ref. 16, applied only to SF_4^- , SF_5^- , and SF_6^- neutralized by Ar^+), plotted vs the electron binding energy of the anion, E_a . The lines shown are power-law least-squares fits. Particular anions may be identified by their E_a values listed in Table I. The theoretical value which lies well above the power law fits (at $E_a = 2.273$ eV) is for $\text{NO}_2^- + \text{Ar}^+$, which has the smallest reduced mass of all the anions on the plot (see Table I). The two experimental data which lie well below the power law fit are for $\text{SF}_4^- + \text{Ar}^+$ (at $E_a = 1.5$ eV) and $\text{SF}_5^- + \text{Ar}^+$ (at $E_a = 4.23$ eV).

accelerates the ions to velocities many times greater than their thermal velocities. The cross section (at energy E) is dominated by an E^{-1} dependence at low energy.^{7,8} The rate coefficient is essentially the average velocity times the cross section, yielding an $E^{-0.5}$ dependence (or $T^{-0.5}$ dependence). Earlier FALP data showed a T dependence consistent with theory; the system $\text{NO}^+ + \text{NO}_2^-$ was studied from 182 to 530 K and gave a $T^{-0.34}$ dependence.⁹ The system $\text{NH}_4^+ + \text{Cl}^-$ was studied from 300 to 430 K and showed a $T^{-0.58}$ dependence.¹³ The bottom line is this: the present data imply

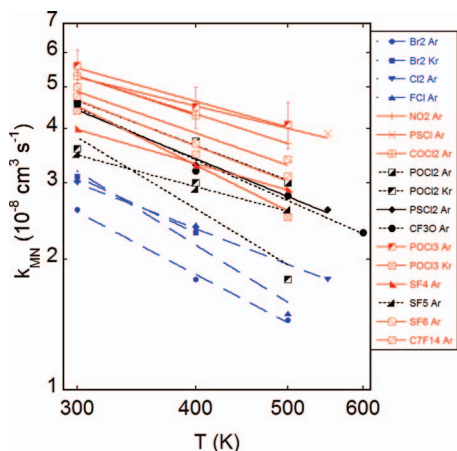


FIG. 2. Log-log plot showing the temperature dependence of k_{MN} for anions neutralized by Ar^+ and Kr^+ . The data are from Table I for anions for which measurements were made beyond 300 K. The straight lines are power law (least-squares) fits to the data. The lowest four lines (dashed, blue) are for diatomic anions. Solid (red) lines are for stable polyatomic anions. Dotted (black) lines are for anions of radical neutrals. Typical absolute error bars are shown for points for the uppermost curve ($\pm 5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$).

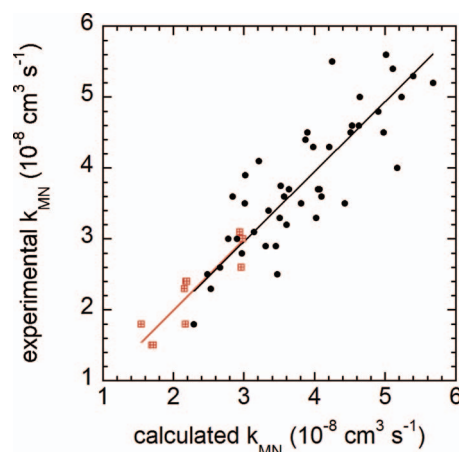


FIG. 3. The present experimental k_{MN} plotted vs evaluations of the parameterizations given in Eqs. (3) (red hatched squares for diatomic anions) and (4) (black solid circles for polyatomic anions), based on a multiparameter fit to the data in Table I at all temperatures.

that the temperature dependence predicted by Landau-Zener theory is too weak. But comparison with the few previous data shows that very precise data are needed to provide a final answer.

Perhaps a better way to examine the T , μ , and E_a dependences is to perform a simultaneous three-parameter fit to all of the data in Table I. For this purpose, the parameterization of Hickman, Eq. (2), was used, but the exponents of T , μ , and E_a were allowed to vary along with the prefactor until the best fit to the data was obtained separately for diatomic and polyatomic anions listed in Table I. Reasonable agreement was found between the parameterization and experiment (usually within $\pm 5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), as shown in Fig. 3, for the following parameterizations, given with fitting uncertainties:

$$k_{\text{MN}} = 3.2 \pm 1.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1} (T/300)^{-1.1 \pm 0.2} \times \mu^{-0.01 \pm 0.09} E_a^{-0.04 \pm 0.23}, \quad \text{diatomic anions, (3)}$$

$$k_{\text{MN}} = 2.8 \pm 1.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} (T/300)^{-0.9 \pm 0.1} \times \mu^{-0.5 \pm 0.1} E_a^{-0.13 \pm 0.04}, \quad \text{polyatomic anions. (4)}$$

For all anions studied, the temperature dependence of k_{MN} is greater than predicted by Landau-Zener theory ($T^{-0.5}$), as was evident in Fig. 2. Likewise, as clear from Fig. 1, the experimental data show a much weaker dependence on E_a than expected from Landau-Zener theory, which had been noted for earlier FALP data.¹⁵ For polyatomic anions, the observed $\mu^{-0.5}$ dependence agrees with theory, but for diatomic anions there is essentially no observable dependence on μ . The fact that the exponents of μ and E_a are practically zero for diatomic anions is a manifestation of the small variation of k_{MN} at a given temperature for the few diatomic anions studied here, which cover ranges of μ (16–55 amu) and E_a (2.3–3.9 eV). The corresponding ranges for the polyatomic anions are $\mu = 21$ –54 amu and $E_a = 1.0$ –4.6 eV.

Because the VENDAMS method allows us to study MN of anions formed from radical neutrals (CN, POCl_2 , PSCl_2 , CF_3O , SF_5 , $\text{Fe}(\text{CO})_4$, and $\text{c-C}_6\text{F}_5$), it is interesting to ask if any difference is seen in the k_{MN} . In Fig. 2, the curves are

labeled differently if the anion was formed from a radical or from a stable neutral. The curves for anions formed from radicals tend to lie lower than those of the stable polyatomics, though higher than the diatomics. CN^- , $\text{Fe}(\text{CO})_4^-$, and $\text{c-C}_6\text{F}_5^-$ were studied only with Ar^+ at 300 K and are thus not shown on the plots showing temperature dependence; their k_{MN} do not add much new information about radicals. Overall, it must be observed that there are not yet enough data to draw any general conclusions about possible differences in k_{MN} for anions formed from radicals or from stable neutrals.

IV. CONCLUSIONS

An intriguing result of our MN work thus far is that k_{MN} for diatomic anions neutralized by Ar^+ and Kr^+ appear rather constant at a given temperature ($3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 300 K), which implies that too few ion-neutral curve crossings are active for application of Olson's absorbing sphere model⁷ or like theories.^{7,16} A more exacting calculation of the location and interaction energy of the particular crossings would have to be carried out to learn the cause of the diatomic anion anomaly. The k_{MN} for the diatomic anions at 300 K lie below those for the polyatomic anions neutralized by Ar^+ and Kr^+ except for $\text{SF}_5^- + \text{Kr}^+$ at 300 K.

We have pulled together our recent MN data obtained with the VENDAMS method to search for correlations with parameters deemed important in the absorbing sphere model,⁷ and to compare results with that theory and Hickman's complex potential extension,⁸ and a similar Landau-Zener calculation of Bopp *et al.* for SF_4^- , SF_5^- , and SF_6^- neutralized by Ar^+ .¹⁶ The temperature dependence (Fig. 2) is fairly clear in following a power law. At the time of this writing, we are finding an exponent that is greater than expected from fundamental expectations, i.e., $T^{-(0.9 \pm 0.1)}$ for polyatomic anions and $T^{-(1.1 \pm 0.2)}$ for diatomic anions neutralized by Ar^+ or Kr^+ , instead of $T^{-0.5}$. A multiparameter fit to the polyatomic anion data yields a reduced mass dependence of $\mu^{-0.5}$ in agreement with theory. Both the T and μ dependence in k_{MN} enter theory through the expected $E^{-0.5}$ energy dependence for a Coulomb interaction at thermal energies. Thus, the T dependence observed in this work suggests that Landau-Zener theory requires modification in the way that it has been applied to curve crossings for systems where a large number of neutral states exist.

In concert with an examination of earlier FALP data, we are finding a weaker dependence on E_a than expected from the absorbing sphere model (Fig. 1), more like $E_a^{-0.1}$ instead of $E_a^{-0.4}$.

The weaker dependences on E_a found here is a reflection of the observation, dating back to the earlier FALP data,⁹⁻¹⁴ that there is not much variation in k_{MN} for polyatomic ions at a fixed temperature, which is a boon to plasma modelers. For experimentalists, it means that accurate data are required to draw general conclusions about the behavior of k_{MN} and for meaningful comparison with theory. Aside from the need for more accurate data, we hope to be able to make measurements for atomic anions neutralized by molecular cations (the opposite of the polarities in the present work). And we look forward to comparison with MN data from the nearly

completed DESIREE facility, which consists of double electrostatic storage rings for merged ion beam studies at about 10 K and variable interaction energies.⁴¹ Given the correlations noted in the present work, especially regarding the diatomic anions studied, it would be helpful if the theory of MN could be re-examined.

ACKNOWLEDGMENTS

This project was funded by the (U.S.) Air Force Office of Scientific Research under Project AFOSR-2303EP. T. M. M. is under contract (Contract No. FA8718-10-C-0002) to Boston College.

- ¹T. M. Miller, J. F. Friedman, and A. A. Viggiano, *Int. J. Mass Spectrom.* **267**, 190 (2007).
- ²J. J. Thomson and E. Rutherford, *Philos. Mag.* **42**, 392 (1896).
- ³L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California, Berkeley, 1955) pp. 477–596.
- ⁴H. S. Lee and R. Johnsen, *J. Chem. Phys.* **90**, 6328 (1989).
- ⁵M. R. Flannery, *Adv. At. Mol. Opt. Phys.* **32**, 117 (1994).
- ⁶M. Stenrup, Å. Larson, and N. Elander, *Phys. Rev. A* **79**, 012713 (2009), and references therein.
- ⁷R. E. Olson, *J. Chem. Phys.* **56**, 2979 (1972).
- ⁸A. P. Hickman, *J. Chem. Phys.* **70**, 4872 (1979).
- ⁹D. Smith and M. J. Church, *Int. J. Mass Spectrom. Ion Phys.* **19**, 185 (1976).
- ¹⁰D. Smith and M. J. Church, *Planet. Space Sci.* **25**, 433 (1977).
- ¹¹M. J. Church and D. Smith, *Int. J. Mass Spectrom. Ion Phys.* **23**, 137 (1977).
- ¹²M. J. Church and D. Smith, *J. Phys. D* **11**, 2199 (1978).
- ¹³D. Smith, M. J. Church, and T. M. Miller, *J. Chem. Phys.* **68**, 1224 (1978).
- ¹⁴D. Smith and N. G. Adams, in *Physics of Ion-Ion and Electron-Ion Collisions*, edited by F. Brouillard and J. W. McGowan (Plenum, New York, 1983).
- ¹⁵T. M. Miller, *J. Chem. Phys.* **72**, 4659 (1980). Equation (2) of this paper has a misprint; the restriction should read $T \leq 1000 \text{ K}$.
- ¹⁶J. C. Bopp, T. M. Miller, A. A. Viggiano, and J. Troe, *J. Chem. Phys.* **129**, 074308 (2008).
- ¹⁷N. S. Shuman, T. M. Miller, C. M. Caples, and A. A. Viggiano, *J. Phys. Chem. A* **114**, 11100 (2010).
- ¹⁸R. Johnsen, E. V. Shun'ko, T. Gougousi, and M. F. Golde, *Phys. Rev. E* **50**, 3994 (1994).
- ¹⁹D. Smith and P. Španěl, *Adv. At. Mol. Phys.* **32**, 307 (1994).
- ²⁰J. F. Friedman, T. M. Miller, J. K. Friedman-Schaffer, A. A. Viggiano, G. K. Rekha, and A. E. Stevens, *J. Chem. Phys.* **128**, 104303 (2008).
- ²¹T. M. Miller, *Adv. At. Mol. Opt. Phys.* **51**, 299 (2005).
- ²²P. Španěl, *Int. J. Mass Spectrom.* **149/150**, 299 (1995).
- ²³N. G. Adams and D. Smith, *Chem. Phys. Lett.* **144**, 11 (1988), and references therein.
- ²⁴P. A. Lawson, D. Osborne, Jr., and N. G. Adams, *Int. J. Mass Spectrom.* **304**, 41 (2011), and references therein.
- ²⁵A. G. Dean, D. Smith, and N. G. Adams, *J. Phys. B* **7**, 644 (1974).
- ²⁶D. Trunec, P. Španěl, and D. Smith, *Contrib. Plasma Phys.* **34**, 69 (1994).
- ²⁷J. F. Friedman, A. E. Stevens, T. M. Miller, and A. A. Viggiano, *J. Chem. Phys.* **124**, 224306 (2006).
- ²⁸N. S. Shuman, T. M. Miller, R. J. Bemish, and A. A. Viggiano, *Phys. Rev. Lett.* **106**, 018302 (2011).
- ²⁹N. S. Shuman, T. M. Miller, J. F. Friedman, A. A. Viggiano, S. Maeda, and K. Morokuma, *J. Chem. Phys.* **135**, 024204 (2011).
- ³⁰N. S. Shuman, T. M. Miller, R. J. Bemish, and A. A. Viggiano, *J. Phys. Conf. Ser.* **300**, 012007 (2011). There is a misprint in Table 2 of this paper: the anion COCl_2^- is mistakenly given as $(\text{COCl})_2^-$.
- ³¹N. S. Shuman, T. M. Miller, A. A. Viggiano, E. D. Luzik, Jr., and N. Hazari, *J. Chem. Phys.* **134**, 044323 (2011).
- ³²N. S. Shuman, T. M. Miller, and A. A. Viggiano, *J. Chem. Phys.* **133**, 234304 (2010).
- ³³N. S. Shuman, T. M. Miller, J. F. Friedman, and A. A. Viggiano, *J. Chem. Phys.* **136**, 124307 (2012).
- ³⁴N. S. Shuman, T. M. Miller, J. F. Friedman, and A. A. Viggiano, "Electron Attachment to $\text{Fe}(\text{CO})_n$ ($n = 0-5$)," *J. Phys. Chem. A* (submitted).

- ³⁵T. M. Miller, J. F. Friedman, N. S. Shuman, S. G. Ard, J. J. Melko, and A. A. Viggiano, "Electron attachment to C_7F_{14} , thermal detachment from $C_7F_{14}^-$, the electron affinity of C_7F_{14} , and neutralization of $C_7F_{14}^-$ by Ar^+ ," J. Chem. Phys. (submitted).
- ³⁶T. M. Miller, in *Handbook of Chemistry and Physics*, 92nd ed., edited by W. M. Haynes (CRC, Orlando, 2011), Sec. 10, pp. 147–166.
- ³⁷L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- ³⁸L. Horný, K. W. Sattelmeyer, and H. F. Schaefer III, *J. Chem. Phys.* **119**, 11615 (2003).
- ³⁹J. Troe, T. M. Miller, and A. A. Viggiano, *J. Chem. Phys.* **136**, 121102 (2012).
- ⁴⁰P. Španěl and D. Smith, *Chem. Phys. Lett.* **258**, 477 (1996).
- ⁴¹R. D. Thomas, H. T. Schmidt, G. Andler, M. Björkhage, M. Blom, L. Brännholm, E. Bäckström, H. Danared, S. Das, N. Haag, P. Halldén, F. Hellberg, A. I. S. Holm, H. A. B. Johansson, A. Källberg, G. Källersjö, M. Larsson, S. Leontein, L. Liljeby, P. Löfgren, B. Malm, S. Mannervik, M. Masuda, D. Misra, A. Orbán, A. Paál, P. Reinhed, K.-G. Rensfelt, S. Rosén, K. Schmidt, F. Seitz, A. Simonsson, J. Weimer, H. Zettergren, and H. Cederquist, *Rev. Sci. Instrum.* **82**, 065112 (2011).