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GASEOUS ION RECOMBINATION RATES. IV

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Gaseous Ion Recombination Rates. IV

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The rates of the bimolecular and termolecular neutralization reactions of gaseous ions generated from the thallium and lead halides have been measured. The absolute values of the termolecular rate constants are generally consistent with Thomson's theory of ion recombination, although the experimental temperature dependence of the rate constant is somewhat greater than the theory predicts. The bimolecular rate constants are consistent with what is known about the energetics and masses of the systems. A mass spectrometric examination of gaseous ion-neutral complex formation is presented.

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In previous papers in this series,[1,2,3] we have established that the neutralization reaction of gaseous ions proceeds by the following mechanism

$$A^+ + B^- \xrightarrow{k_o} \text{neutrals}$$

$$A^+ + B^- \xrightarrow{k_1} (A^+B^-)^*$$

$$(A^+B^-)^* \xrightarrow{k_2} A^+ + B^-$$

$$M + (A^+B^-)^* \xrightarrow{k_3} (A^+B^-) + M \rightarrow \text{neutrals}$$

Here $(A^+B^-)^*$ represents a pair of unbound ions close enough to each other so that a collision of either of them with a neutral molecule M leads to formation of a bound ion pair (A^+B^-) and eventual charge neutralization. In the systems we have investigated previously,[1,3] the ions have been molecular, some of rather complex structure. While negative ions with a variety of electron affinities have been involved, the positive ions investigated have all been derived from molecules with almost identical ionization energies. The present work with the lead and thallium halides was undertaken in an attempt to study systems in which the recombining ions were of simple structure and had electron affinities, ionization energies, and masses quite different from those encountered earlier. This intent was in large measure realized, and in addition, we were able to determine the temperature dependence of the ion recombination rate over a range of 240°K.

In our experiments, ions were produced by pulse photolysis of gaseous lead and thallium halides with light from a spark between zinc or aluminum electrodes. Terenin and Popov[4] first discovered that photolysis of the vapors of thallium and lead halides with 2000 Å radiation produces charged fragments and by energetic considerations and crude mass spectrometry they showed that Tl^+ and I^- were formed in the primary process. Recent work of Berkowitz and Chupka[5] on the photoionization mass spectrum of TlI, as well as our own mass spectrometric work, confirms the findings of Terenin and Popov.

In order to measure the ionic recombination rates, we used the charge collection technique that we have described in detail in an earlier paper.[1] The reaction cell used in the present work was constructed of quartz, but otherwise was identical to the one previously described. The cell was enclosed in a thick-walled aluminum box which itself was enclosed in an oven. Both the oven and aluminum box were equipped with quartz windows coaxial with the cell, so that both the photolysis light source and a photomultiplier that monitored the light which passed through the cell could be located outside the oven. The sample of metal halide was contained in an appendix tube whose temperature was regulated by a Hallikainen Thermotrol unit which has a temperature sensitivity of 0.001°K. The main oven and reaction cell were usually maintained at a temperature 20 to 50°K higher than the appendix tube in order to prevent vapor from condensing on the cell windows. The cell could be

isolated from the vacuum system by a magnetically controlled, greaseless ground-glass valve.

The thallium halides were obtained from the Cooper Chemical Company, New Jersey, and had a stated purity of at least 99.9%. The lead iodide was Mallinkrodt CP grade, and the lead bromide was purchased from Rocky Mountain Research Company, Colorado, and had a stated purity of 99.99%. The argon and xenon used were better than 99.9% pure.

The light source consisted of a pair of zinc or aluminum electrodes enclosed in a separate grounded metallic box equipped with a quartz window. The box was flushed with argon to lower the breakdown potential of the spark gap, and to enhance the intensity of light emitted in the 2000 Å region. Usually a 1 mfd capacitor charged to 6000-8000 volts provided sufficient light intensity. Light from the spark passed through the reaction cell and then onto a photomultiplier. The integral of the signal from the photomultiplier was displayed on an oscilloscope, thus enabling us to measure the intensity of each spark. To assure a constant initial ion concentration, only those sparks with a previously determined standard intensity were used to collect rate data.

After the light pulse from the spark discharge had produced ions, an ion collection voltage was applied at a predetermined delay time to parallel plate electrodes in the cell. The current collected was integrated electronically and displayed on an oscilloscope. The charge collection circuit was designed

so that any false collection current due to the capacitance the electrodes and leads did not appear in the integrated signal. To obtain the recombination rate at a particular temperature and pressure, the charge remaining in the cell was measured at delay times ranging from a few milliseconds to approximately one second, at which time the ion concentration approached 10^6 cm^{-3}, the limit of sensitivity of the apparatus.

RESULTS

A. Determination of the Recombination Rate Constants

Some typical concentration-time data are shown in Fig. 1. If the ions disappeared exclusively by homogeneous bimolecular and termolecular processes, a plot of reciprocal ion concentration as a function of time would be linear. It is clear that the data of Fig. 1, as well as all other data we collected, deviate from linear behavior in a manner that suggests a competitive first order ion loss process. This first order decay process becomes less important at the higher inert gas pressures, and can be attributed to diffusional loss of ions to the walls. The higher temperatures employed in this work (480-730°K) decrease the ion recombination rate, and increase the diffusional loss rate, so that diffusion is a much more serious problem in these experiments than in the earlier work[1,3] done at 300°K.

To extract the value of α, the second order ion recombination coefficient, the data might be analyzed in terms of the equation

$$-dn/dt = \alpha n^2 + \beta n$$

where n is the ion concentration, and the terms on the right represent homogeneous recombination and diffusional loss, respectively. This equation is only appropriate when one of the loss terms dominates the other, which was often not the case in our work. Values of α obtained using this equation differed by 10-20% from those determined with a more accurate analysis described below.

Another approximate description of the ion loss process follows from the assumption of one dimensional ambipolar diffusion, and can be expressed as

$$-\frac{\partial n}{\partial t} = \alpha n^2 - D_a \frac{\partial^2 n}{\partial x^2} \qquad (1)$$

where x is the distance from the midpoint of two infinite parallel planes, and D_a is the ambipolar diffusion coefficient given by

$$D_a = 2D^+D^-/(D^+ + D^-)$$

where D^+, D^- are the diffusion coefficients and of the positive and negative ions. Equation (1) was solved numerically with values of the parameters appropriate to our system, and the predicted ion concentration as a function of time was compared to that derived from numerical solution of the exact loss equations for the positive and negative ions separately. In the concentration range employed in our experiments, the

ambipolar approximation gave results that agreed with the predictions of the exact equations to within better than one percent. Consequently, Eq. (1) was used to analyze all our data. A value of D_a for a particular temperature and halide-inert gas combination was determined from a run at low pressure where diffusion was dominant. The diffusion coefficient was found to be inversely proportional to inert gas density, and a value of α was obtained for each run by a trial and error fit of Eq. (1) to the experimental data. The smooth curves of Fig. 1 are calculated from Eq. (1) with the best fit parameters and agree well with the experimental data points. Variations in α of approximately $\pm 0.1 \times 10^{-8}$ cc/sec produced noticeable deviations of the calculated curve from the experimental points. The values of α obtained in this manner are given in Table I.

From the mechanism for ion recombination, we expect the equation

$$\alpha = k_o + k_1 k_3 [M]/(k_3 [M] + k_2)$$

to hold. In the low density regime where our experiments were performed, the relation $k_3[M] << k_2$ is satisfied, and we expect the density dependence of the recombination coefficient to be given by

$$\alpha = k_o + (k_1 k_3/k_2)[M].$$

Figure 2 shows α plotted as a function of [M] for some of the data. The intercept is independent of the nature of the inert gas, but characteristic of the halide system, as one would

expect if k_o represents the rate constant of the bimolecular process. In addition, the slope of the α-[M] plots is dependent both on the nature of the inert gas and the halide, as expected for the rate constant of the termolecular process. Values of the rate constants obtained from such graphs are given in Table II.

In a number of runs, TlI was photolysed in the presence of a small amount (0.08 Torr) of NO_2, in the hope that the reaction

$$NO_2 + I^- \rightarrow I + NO_2^-$$

would occur, and the recombination of Tl^+ and NO_2^- could be studied. As will be shown later, the principal negative ion in this system contains nitrogen, but is not NO_2^-. In any case, the recombination rate constants for the systems TlI and TlI-NO_2 are different, as the data in Table II show.

A series of experiments was performed in order to determine the temperature dependence of the ion recombination rate constant. The system studied was TlI-Xe, all experiments were carried out at a constant pressure of 176 ± 1 Torr, and the temperature was varied from 484°K to 728°K. The results are reported in Table III.

B. The Nature of the Ions

In an attempt to determine the nature of the ions present in the kinetic experiments, we used a small, 12-stage radio frequency mass spectrometer of the type described by Boyd and

Morris[6] to sample the ions produced by the continuous photolysis of TlI vapor by the light (2062 Å) from a microwave excited atomic iodine lamp. The results are given in Table IV. With TlI alone at 630°K and 0.04 Torr, the only ions observed were Tl^+ and I^-, while ions whose intensity was 0.002 times as large could have been detected. This result is consistent with the work of Berkowitz and Chupka,[5] and establishes the nature of the primary photo-ions.

In order to simulate the conditions under which the kinetic experiments were done, experiments were done with an inert gas present in the photoionization source of the mass spectrometer. Sulfur hexafluoride was used because of its inert nature and because it could be pumped cryogenically, thereby allowing the analyses of the mass spectrometer to be maintained at a low pressure. In the second column of Table IV are the ions observed when 1 Torr of sulfur hexafluoride was present with 0.04 Torr TlI in the photolysis cell. Under these conditions the ions Tl_2I^+ and TlI_2^- appear, apparently because they are formed by termolecular reactions, for example

$$Tl^+ + TlI + SF_6 \rightarrow Tl_2I^+ + SF_6,$$

that are not possible at the lower total pressures. Under our experimental conditions, the product of concentrations $[TlI][SF_6]$ was 10^{31} (molecules)^2/cm^6, and the ions remained in the high pressure region for approximately 10^{-3} sec. Since the complexed ion is 0.1 times as intense as the primary ion, we estimate the rate constant for the termolecular association as

approximately 10^{-29} cm^6/sec at 630°K. This rate constant is about 100 times larger than measured rates[7] for atom-atomic ion association reactions. However, the increased complexity and consequently longer lifetime of the initial ion-molecule collision complex, as well as the larger collision cross sections for formation and deactivation in the Tl^+-TlI system are sufficient to account for this difference in rate constants.

When the temperature of the mass spectrometer source was raised to 720°K, the thallium iodide vapor pressure increased to 1 Torr, the complexes Tl_2I^+ and TlI_2^- became the dominant ions, and the double complexes $Tl(TlI)_2^+$, $T(TlI)_2^-$ were observed in small amounts, as shown in Table IV. The double complexes could be formed by either of the reactions

$$Tl_2I^+ + 2TlI \rightarrow Tl_3I_2^+ + TlI$$

$$Tl^+ + (TlI)_2 + TlI \rightarrow Tl_3I_2^+ + TlI$$

The former seems more likely to be important, since Tl_2I^+ is in abundance, and Cubicciotti[8] has estimated that the dimer concentration in pure thallium iodide vapor is less than 1% of the monomer at total pressures between 1 Torr and 1 atm.

Mixtures of nitrogen dioxide with thallium iodide vapor were also examined mass spectrometrically. At a thallium iodide pressure of 0.04 Torr, and a nitrogen dioxide pressure of approximately 0.07 Torr, the only positive ions observed were Tl^+ and $Tl_2NO_3^+$, while the negative ions were I^-, NO_3^-, and

$Tl(NO_3)_2^-$ in order of decreasing abundance. A careful search for NO_2^- was made, since we expected the reaction

$$I^- + NO_2 \rightarrow NO_2^- + I$$

to occur, but no NO_2^- was detected in any of our experiments.

When the gaseous NO_2 was removed from the photoionization chamber, but the sample of solid TlI which had been in contact with NO_2 retained, the ions Tl^+, I^-, and NO_3^- were observed upon photolysis, as indicated in column 4 of Table IV. When SF_6 at 1 Torr pressure was added, the ions $Tl_2NO_3^+$, $Tl(NO_3)_2^-$ reappeared. These observations suggest the complex ions are formed from Tl^+ and NO_3^- associating with $TlNO_3$ vapor, which itself is the product of some reaction of NO_2 with solid TlI. To explore this idea further, the mass spectrometer was cleaned, and then a charge of pure solid $TlNO_3$ was vaporized at 630°K. No ions were observed upon photolysis. When TlI was added to the $TlNO_3$, the ions in column 6 of Table IV were observed. The appearance of $Tl_2NO_3^+$ and $Tl(NO_3)_2^-$ as well as NO_3^- under these conditions suggest the occurrence of the reactions

$$I^- + TlNO_3 \rightarrow TlI + NO_3^-$$

$$NO_3^- + TlNO_3 \rightarrow Tl(NO_3)_2^-$$

$$Tl^+ + TlNO_3 \rightarrow Tl_2NO_3^+$$

The latter two reactions require a third body to deactivate the complex ion. The fact that they are observed at all at our rather low ion source pressures is probably due to the many degrees of freedom of the collision complex which prolong its life and make eventual deactivation possible.

Experiments in which NO_2 was added to TlI vapor which itself was at 1 Torr pressure and 720°K were performed. Table IV shows that the new ions formed under these conditions were $(TlI)_2NO_3^-$ and $TlINO_3^-$. Some very small amounts of I^+ and TlI_2^+ were also observed. The origin of these ions is difficult to ascertain, but we feel they may have been formed by impact of photoelectrons that had been accelerated by the mass spectrometer electrode system.

In the ion recombination experiments, the thallium iodide pressure was usually less than 0.01 Torr, but the inert gas pressure was always greater than 30 Torr. Thus the mass spectrometric observations show that complex ions should be formed rapidly (10^{-3} sec) compared to the characteristic minimum delay time of about 0.01 sec, after which most of the rate data were obtained. The mass spectrometer data also suggest that the complex ions Tl_2I^+ and TlI_2^- should be present in important, and very likely in dominant concentration in the recombination experiments. For the $TlI-NO_2$ system, the ions $Tl_2NO_3^+$ and $Tl(NO_3)_2^-$ are of greatest importance.

Attempts were made to investigate the ions in other thallium and lead halide systems mass spectrometrically. All these experiments were unsuccessful because low ion concentration made mass descrimination and identification impossible. However, it appears reasonable to conclude that if ions of the type M_2X^+ and MX_2^- are important in the thallium iodide system, they will be at least as important in the thallium bromide and chloride systems as well. Calculations of the equilibrium

constant[9] for formation of M_2X^+ and MX_2^-, based upon an ion-induced dipole and ion-permanent dipole interaction support this conclusion. These calculations, admittedly uncertain because of difficulties in estimating the interaction energy accurately, suggest that atomic and complexed ions should be of comparable importance in the TlI system, and that complexed ions are 10^3 to 10^7 times more abundant than atomic ions in the TlBr and TlCl systems.

Information concerning the nature of the ions can be drawn from the diffusion coefficients determined experimentally from the ion decay rates. One can expect the diffusion coefficients for atomic ions and the much heavier and larger complex ions to be different enough so that a comparison of the experimental diffusion coefficients with those calculated for the various types of ions will be meaningful. Table V gives experimental and calculated values of the constant C defined by $C = (N/T)D_a$, where N is the particle density, T is the temperature, and D_a is the ambipolar diffusion coefficient. The calculations were made with the Sutherland type of intermolecular potential which occurs in the Langevin ion mobility theory.[10] In this potential there is a long range attractive term due to the ion-induced dipole interaction and a rigid sphere core repulsion. For the atomic ions we took the core radius as the sum of the ionic and atomic radii of ion and inert gas atom, respectively. For the complex ions in the thallium halide systems we assumed a linear symmetric geometry with internuclear distance chosen two ways: (a) as equal to

that in the free TlX molecule, and (b) equal to the crystal lattice spacing. These internuclear distances, together with the ionic radii, allowed us to define the dimensions of a spherocylindrical molecule, and from this an angle-average radius was computed for the ion.

It is seen from Table V that the calculated ambipolar diffusion coefficients for the Tl_2X^+, TlX_2^- ions are nearly in agreement with experiment, while those calculated for the atomic ions are clearly too large. The experimental diffusion coefficients are thus consistent with our earlier conjecture that the ions in dominant concentration are Tl_2X^+ and TlX_2^-.

There is no direct experimental information about the nature of the primary ions in the lead halide systems. One might assume that PbX_2 is photodissociated to PbX^+ and X^-, but it is also possible that the source of ions is the photolysis of PbX, which is formed by

$$PbX_2 = PbX + X$$

Calculations of the equilibrium constants for these reactions using tabulated bond energies,[11] and making reasonable assumptions concerning the geometry of PbX_2 show that the ratio $[PbX]/[PbX_2]$ is 4×10^{-5} for PbI_2 and 2×10^{-6} for $PbBr_2$ under our experimental conditions.[12] It seems safe, therefore, to assume that the ions are formed as a result of the photolysis of the parent PbX_2 molecules.

Because the geometries and dipole moments of the lead halides are now known with certainty, calculations of the

equilibrium constant for association of ions with them can have only qualitative significance. Nevertheless, calculations were performed using the estimated values of the necessary parameters, with the result that the predicted concentration ratios $[Br^-]/[PbBr_3^-]$ and $[PbBr^+]/[PbBr_3^+]$ were near unity for our experimental conditions at 707°K. For the lead halide system, the ratio $[I^-]/[PbI_3^-]$ was calculated to be 36, while $[PbI^+]/[Pb_2I_3^+]$ was noticeably smaller, 3×10^{-3}. This latter result is mostly a consequence of being able to choose for $Pb_2I_3^-$ a geometry in which the positive end of the PbI^+ dipole interacts strongly with both iodine atoms of PbI_2. These results, while by no means conclusive, at least suggest that the majority of ions need not be complexed in the lead halide systems at the temperatures and pressures at which we worked. For further information we turned to interpretations of the experimental ambipolar diffusion parameters.

Calculations of the diffusion constants of PbX^+, $Pb_2X_3^+$, X^-, and PbX_3^- were carried out using the Langevin formula with a hard core radius. Since the geometries of the ions PbX_3^- and $Pb_2X_3^+$ are unknown, we chose for them a "radius" that was independent of geometry by using the expression

$$r_{ion} = \left(\sum_i r_i^2 \right)^{1/2}$$

where the sum is over each atom in the complex ion. Two sets of radii were used. One set reproduced the lead halide crystal distances, and in the other set, the radius of Pb^{2+} was

decreased so as to reproduce the bond distances of the gas phase PbX_2 molecules.

The results of the calculations are given in Table V, where C_1 is obtained using the larger, and C_2 the smaller radius for Pb^{2+}. For the lead iodide system, the best agreement between calculation and experiment obtains when one ion but not the other is complexed. Another possible interpretation is that both positive and negative ions are partly complexed and partly free, but in view of the difference in geometry and charge distribution in I^- and PbI^+, the first alternative seems the more likely. In either case, complex ions are important in the lead iodide system at 594°K.

For the lead bromide system, the calculated diffusion parameters for the free ions $PbBr^+$ and Br^- are only 3% higher than experiment. If either ion is assumed to be complexed, the calculated diffusion parameters are roughly 20% too small. Thus for the lead bromide system at 707°K, it appears that neither $PbBr^+$ nor Br^- is complexed to $PbBr_2$ to any appreciable extent.

DISCUSSION

A. Bimolecular Rate Constants

Mutual neutralization by the bimolecular process is thought to involve a collision that brings the two ions to a separation at which the Coulomb potential energy is equal to the energy of another electronic state which can dissociate to neutral fragments. If the location of the potential energy

curve crossings, and the probability of making a transition from one curve to the other were known, the bimolecular neutralization rate could be calculated. Such calculations have been carried out for atomic ions by Bates and Boyd.[13]

To discuss bimolecular recombination in the thallium iodide system, we can use the potential energy curves of the diatomic molecule as a point of departure. Figure 3 shows some of these curves for TlI. Crossings of the "ionic" curve with the "covalent" curves occur at approximately 7 Å and 13 Å as well as smaller distances. These crossing points would be expected to be the important ones for the recombination of the free atomic ions Tl^+ and I^-.

We can now consider what modifications must be made in the potential energy diagram when Tl^+ and I^- become the complexes $Tl^+(TlI)$ and $I^-(TlI)$. At the very least, the asymptotic energy of the ionic state is lowered by the sum of the energies released in forming the complexes from the free ions and neutral molecules. We might also expect that to a first approximation, the whole ionic curve would be lowered by the same amount of energy. The potential energy curves of the covalent states of TlI should be changed relatively little at great internuclear distances by complexing the atoms with diatomic molecules, since the interaction between the neutral atom and the diatomic molecule is largely due to weak dipole-induced dipole and London effects. For the thallium halides our calculation of the ion-neutral complex energy using ion-dipole and ion-induced dipole terms suggests the lowering of the ionic curve is great

enough ($\approx$ 2 eV) so that the only covalent curve that is crossed at large separation belongs to the ground state of TlX. This is indicated in Fig. 3.

Because of the uncertainty in the energy released in ion complex formation it is impossible to predict the location of the crossing point of the ionic and covalent curves. It is instructive, however, to reverse the procedure and obtain from the measured rate constants an estimate of the crossing point location. If the criterion for bimolecular neutralization is that the centers of mass of the ions reach a separation equal to or less than ρ, the corresponding rate constant is[1]

$$k_o = \pi\rho^2(8kT/\pi\mu)^{1/2}\ (1 + e^2/\rho kT) \qquad (2)$$

where μ is the reduced mass, e is the fundamental charge, and k is Boltzmann's constant. Table VI contains the values of R derived from the experimental rate constants by using this equation. The values obtained lie in the range of 10 to 20 Å, and are thus somewhat smaller than those obtained earlier for other systems.[1,3] It should be noted, however, that the idea of a unique crossing point for ionic and covalent curves is a considerable simplification when we are dealing with molecular ions. First, the slope of the ionic curve in the region around 20 Å is only 0.04 eV/Å, and that of the covalent curve essentially zero, so that the two curves are close to each other over a substantial range of internuclear separation. In addition, changes in the excitation of internal degrees of freedom of the complex ions could change the location of the crossing point on the one-dimensional diagrams.

Because the ions $PbBr^+$ and Br^- were present as free species in the recombination experiments, it would seem possible to make a meaningful comparison between the experimentally determined ionic-covalent crossing point, and that estimated from the energetics of the lead bromide system. Unfortunately, the ionization energy of PbBr is not known, and consequently it is only possible to make a crude estimate of the crossing point from the energetics. An examination of the ionization energies[11] of a few other monohalides of the lighter group IV elements shows them to be less than the ionization energy of the metal by 0.5 to 1 eV, with the difference decreasing as the atomic numbers of the metal and halide increase. This suggests the assumption that the ionization energies of Pb and PbBr are equal, and leads to the conclusion that the state $PbBr^+$, Br^- lies 4 eV above the energy of the fragments PbBr, Br. We also know that $PbBr_2$ is photodissociated into ions by light with wavelengths between 2100 Å and 1800 Å, and this combined with a bond energy[11] of 2.9 eV for $PbBr_2$ indicates that the ions lie between 3 and 4 eV above the ground states of the fragments PbBr and Br.

The known[14] excited states of PbBr lie at 2.6 and 4.3 eV, and it appears that only the first of these lies below the energy of the ion fragments. The bromine atom has an excited state 0.46 eV above its ground state, and consequently the energy of the fragments $PbBr^*$, Br, and $PbBr^*$, Br^* lie 1.4 and 0.9 eV below the energy of the separated ions. Using the expression $\rho = e^2/\Delta E$ then gives the crossing points as 11 and

17 Å, respectively. These values bracket the result of 14 Å derived from the rate data. Because of the uncertainty in the ionization energy of PbBr of perhaps ±0.3 eV, values of the crossing points ranging from 9 Å to 25 Å might have been predicted. Until this uncertainty is removed it will not be possible to interpret the value of the bimolecular rate constant more precisely. At present it is possible only to say that its magnitude is consistent with what is known about the energetics of the system.

B. Termolecular Rate Constants

The simplest theories of three-body ion recombination involve the idea of a capture radius introduced by J. J. Thomson.[15] Thomson proposed that if one of a pair of ions that had approached closer to each other than some critical distance were to collide with a neutral molecule, the ions might lose enough relative kinetic energy to become bound to each other. On essentially intuitive grounds, Thomson took the critical distance to be $R_c = e^2/[(3/2)kT]$, or the distance at which the relative kinetic energy of the ions had increased by an amount equal to their average initial energy. The probability that either ion would collide with a neutral while within this critical separation was calculated after making some simplifying assumptions, and a termolecular rate constant obtained. Mahan and Person[1] showed that Thomson's theory was in good numerical agreement with a substantial amount of experimental data. Subsequent refinements of Thomson's theory by Natanson[16] and

Brueckner[17] have involved more rigorous methods of choosing the critical radius. Brueckner's treatment in particular led to a much reduced value of R_c, and resulted in calculated rate constants that are much smaller than those found experimentally. Numerical calculations of ion recombination constants by Mahan and Person[2] and by Feibelman[18] showed that considerable contributions to the rate were made by configurations in which the ions were separated by distances greater than the critical radius R_c, and that collisional redissociation of weakly bound ion pairs is important. Bates and Moffet[19] used an entirely different theoretical approach to the problem in which the concept of a critical radius does not enter, but found rate constants that were essentially the same as those calculated from the Thomson theory. The present situation seems to be that the original Thomson theory with its prescribed choice of the critical radius is in good numerical agreement with experiment and with an essentially exact theory, but it is impossible to justify its details by using classical molecular mechanics. Thus while the idea of a unique capture radius cannot be a central part of a fundamental theory of ion recombination, simple theories based on it may be useful numerically.

To illustrate this point, we note that Thomson's expression for the termolecular rate constant is

$$k_t = (128/81)(2\pi/\mu)^{1/2}\ e^6(kT)^{-5/2}[(1/\ell^+) + (1/\ell^-)]\ N^{-1}$$

where N is the concentration of inert molecules, ℓ^+ amd ℓ^- are the mean free paths of the ions, k is Boltzmann's constant, e is the fundamental charge, and T is the absolute temperature.

If the masses of both ions are greater than the mass of the neutral molecules, one can write

$$1/\ell^{+} + 1/\ell^{-} \cong (2/3)(8kT/\pi m)^{1/2}\, D_a^{-1}$$

where m is the mass of the neutral, and D_a is the ambipolar diffusion coefficient. It is therefore possible to evaluate the mean free path function from the experimentally measured diffusion coefficient, and calculate the rate constant using Thomson's expression. Table VII gives the comparison of the rate constants so calculated with the experimental data. In general, the agreement is quite good. The numerical success of the Thomson theory is particularly impressive when one considers that the theory is also in agreement with rate constants one order of magnitude larger which were measured at lower temperatures for lighter ions.

The Thomson theory and its refinements were designed for cases in which the recombining ions have equal masses. This condition is violated in the experiments reported in this paper, in one case quite seriously. Consequently before a detailed comparison with theory is made, the theory should first be extended to include the case of unequal ionic masses. Such an extension of Bruechner's theory has been accomplished, and will be reported and compared with experimental data in a subsequent paper. Here we will make some qualitative observations about the termolecular rate constants.

Examination of the results in Table VII shows that for each halide system xenon is a better third body than argon. This is to be expected from previous experimental results,[1,3] and from the more fundamental consideration of collision cross section and kinematic factors. The Thomson theory reproduces this effect successfully.

The recombination rate constants in the TlBr, TlCl, $TlI-NO_2$, and PbI_2 systems are nearly the same for a given inert gas. This is also to be expected if one considers that the sizes and masses of the ions are all large, and exhibit a fairly small relative variation from system to system. The Thomson theory is in accord with this behavior. The rate constants for the TlI system are somewhat higher than expected on this basis. This deviation might be a result of the presence of some free atomic ions. The opposite deviation occurs in the $TlI-NO_2-Ar$ system where the Thomson theory predicts a higher rate constant than is observed. The explanation for this deviation is not known.

It should be noted that the correlation between the ambipolar diffusion coefficient and the recombination rate constant may break down when the ion masses differ substantially. The ambipolar diffusion coefficient may be dominated by the heavier, slower ion, while most of the collisions that lead to recombination will involve the light ion. This situation occurs in the $PbBr_2$ system where the bromide ion is much lighter than $PbBr^+$, and the measured rates of recombination are larger than expected from the diffusion constant. For this system also the ratio of the rate constants for argon and xenon is larger than

for any other system, which is expected if most of the deactivations involve collisions with the relatively light bromide ion. In summary, it appears that the termolecular rate data can be correlated qualitatively with ambipolar diffusion coefficients through the Thomson theory when the ion masses are similar, but some quantitative variations in the rate constants occur.

C. Temperature Dependence

The temperature dependence of the recombination rate was studied in order to check the predictions of the Thomson theory. The results for the thallium iodide system are summarized in Table III and Fig. 4. In order to find the temperature dependence of the termolecular process, it is necessary to subtract the bimolecular rate constant from the measured pseudo-second order rate. This was done by using the observed value of k_o at 531°K to calculate a value of ρ to be used in Eq. (2), which was in turn used to predict the small temperature variation of k_o. The recombining ions were again taken as Tl_2I^+ and TlI_2^-. The resulting temperature dependence of the third order rate constant is shown as a log-log plot in Fig. 4.

Figure 4 shows that at least below about 650°K the third order rate constant decreases as temperature increases approximately as $T^{-4.1}$. If Thomson's expression for the third order constant is written as

$$k_t \propto \pi R_c^3 \, \bar{c} \, (\sigma^+ + \sigma^-)$$

where σ^+, σ^- are the ion-neutral collision cross sections, R_c is the capture radius, and $\bar{c}$ is an average speed, one sees that since R_c varies as $1/T$, and $\bar{c}$ as $T^{1/2}$, k_t varies as $T^{-5/2}$ for an assumed hard sphere ion-neutral interaction. If scattering by the ion-neutral polarization potential is dominant, k_t should vary as T^{-3}. It does not seem possible to duplicate the observed $T^{-4.1}$ dependence using the Thomson theory. This discrepancy may be an indication of the shortcomings of the Thomson theory. However, the intrinsic experimental uncertainty, together with the possibility that our method of correcting for bimolecular contribution is inadequate, suggest that this conclusion cannot be firm. An additional complicating factor is the possibility that the fraction of ions that are complexed may vary over the temperature range. If the fraction of free ions increases as temperature increases, the apparent rate will decrease more slowly than the true rate constant. This effect may be responsible for the deviation of the data at temperatures near 700°K from the straight line in Fig. 4. If any appreciable effect of this kind is operative over the whole temperature range, the discrepancy between true temperature dependence of the rate constants and prediction of the Thomson theory is increased.

CONCLUSION

The experimental results reported in this paper, together with the results obtained earlier[1,3] show that the Thomson theory of termolecular ion recombination in its original form

can be used to predict, with semiquantitative success, recombination rate constants even though the ion and neutral masses and sizes, as well as temperature, may vary considerably from reaction to reaction. The temperature dependence of the termolecular rate constant found experimentally is somewhat more extreme than the prediction of the Thomson theory, and may constitute an indication of how the theory should be refined.

The bimolecular rate constants found in this work are noticeably smaller than those characteristic of lighter ions derived from molecules of higher ionization energy. The major block to interpretation and prediction of the bimolecular rate constants is the lack of knowledge of the electronic energy levels, ionization energies, and electron affinities of the recombining species.

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Table I. Recombination Coefficient

Pressure (Torr)	Temperature (°K)	$\alpha \times 10^8$ (cm^3/sec)	Pressure (Torr)	Temperature (°K)	$\alpha \times 10^8$ (cm^3/sec)
	TlI-Ar			TlI-Xe	
78	530	6.0 ± .3	34	533	6.5 ± .4
139.5	531	7.3 ± .4	47	530	6.5 ± .4
193	531	9.5 ± .6	71	533	8.0 ± .5
269	531	10.5 ± .6	95.5	532	9.5 ± .4
354	528	12.4 ± .4	117.5	533	10.0 ± .5
			144	523	12.0 ± .6
			160	531	12.5 ± .5
			190	513	14.5 ± .7
			240	530	18.0 ± .8
	TlBr-Ar			TlBr-Xe	
54.5	591	5.5 ± .4	38	593	6.5 ± .3
107	591	7.3 ± .5	74	593	7.2 ± .3
147	561	8.0 ± .7	98.5	596	8.3 ± .4
186	591	9.0 ± .6	126	593	9.0 ± .3
226	561	9.0 ± .7	136.5	596	9.5 ± .3
308	561	10.0 ± .5	178	547	11.5 ± .7
394	561	11.5 ± .8	222	547	13.5 ± .7
	TlCl-Ar			TlCl-Xe	
210	608	9.5 ± .5	48.5	620	7.0 ± .4
300	619	9.75 ± .5	56	613	7.0 ± .5
304	606	11.0 ± .7	68	613	7.3 ± .5
354.5	608	11.0 ± .6	99.5	621	8.5 ± .6
432	610	12.5 ± .5	150	622	10.0 ± .5
			156	616	10.0 ± .5
			191	610	10.6 ± .4
			237	612	11.0 ± .6
			279	603	12.5 ± .7
	$TlI-NO_2-Ar$			$TlI-NO_2-Xe$	
55.5	547	6.0 ± .4	42	554	6.5 ± .3
104	555	6.75 ± .4	49	555	6.75 ± .4
150	548	7.3 ± .4	72	555	7.75 ± .5
199	554	7.7 ± .4	73	553	7.8 ± .4
296.5	548	9.2 ± .5	76	548	7.25 ± .5
			99	555	8.75 ± .6
			110	553	8.0 ± .5
			150	555	9.4 ± .5
			152	553	10.2 ± .6
			152.5	548	10.0 ± .6
			186	558	10.5 ± .5
			198	556	10.5 ± .5

(Continued)

Table I. (Continued)

Pressure (Torr)	Temperature (°K)	$\alpha \times 10^8$ (cm^3/sec)	Pressure (Torr)	Temperature (°K)	$\alpha \times 10^8$ (cm^3/sec)
	PbI_2-Ar			PbI_2-Xe	
77.9	594	4.8	52.7	595	5.0
109.5	593	5.3	73.5	595	6.1
192.4	594	6.4	101.1	593	6.7
251.5	595	7.6	152.8	593	8.1
294.0	595	7.9			
395.0	594	8.8			
	$PbBr_2$-Ar			$PbBr_2$-Xe	
106.2	707	7.5	50.0	707	6.7
202.2	706	9.5	104.0	707	8.2
299.5	707	11.5	151.4	707	9.5
405	707	13.5			

Table II. Termolecular and Bimolecular Rate Constants

System	(Xe) $k_t \times 10^{27}$ [a] (cm^6/sec)	(Ar) $k_t \times 10^{27}$ (cm^6/sec)	$k_o \times 10^8$ ($cm^3\ sec^{-1}$)
TlI	30.4	13.0	4.0
TlBr	19.6	10.6	5.1
TlCl	17.6	11.8	5.6
$TlI-NO_2$	18.6	7.4	5.3
PbI_2	19.1	9.3	3.7
$PbBr_2$	20.6	15.3	5.3

a. The constant $k_t = k_1k_3/k_2$.

Table III. Temperature dependence of recombination coefficient α for thallium iodide in xenon.[a]

Pressure	Temperature	$\alpha \times 10^{-8}$ (cm^3/ion·sec)	$k_t \times 10^{26}$ (cm^6/ion^2 sec)
175.1	484	21	4.79
176.7	489	17.5	3.84
176.9	500	16.7	3.66
177.0	523	13.6	2.94
177.2	553	11.9	2.55
177.4	580	9.1	1.76
177.3	603	8.1	1.52
177.1	627	8.0	1.58
176.1	651	7.3	1.37
177.0	673	7.4	1.50
176.9	696	7.3	1.50
176.8	702	7.5	1.60
176.9	728	7.1	1.53
177	493	14.5	2.98
176	499	14.0	2.88
177	531	14.0	3.08
177	545	13.25	3.0
177.5	571	11.5	2.6
177	605	9.5	2.0
176.5	610	11.0	2.6

[a]The third order constant k_t is obtained from α after subtracting a temperature adjusted value of k_o derived from Eq. (2), as described in the text.

Table IV. Ions Observed Mass Spectrometrically.[a]

TlI	TlI, SF_6	TlI, NO_2	Remove NO_2	Add SF_6	TlI, $TlNO_3$
		Experiments Performed at 630°K			
Tl^+	Tl^+ (100)	Tl^+ (2)	Tl^+	Tl^+ (1)	Tl^+ (10)
	Tl_2I^+ (10)	$Tl_2NO_3^+$ (1)		$Tl_2NO_3^+$ (1)	$Tl_2NO_3^+$ (1)
I^-	I^- (100)	I^- (1)	I^- (2)	I^- (2)	I^- (10)
	Tl_2I^- (1)	NO_3^- (2)	NO_3^- (1)	NO_3^- (2)	NO_3^- (20)
		$Tl(NO_3)_2^-$ (3)		$Tl(NO_3)_2^-$ (7)	$Tl(NO_3)_2^-$ (10)
		Experiments performed at 720°K			
Tl^+		Tl^+ (50)	Tl^+ (230)		
Tl_2I^+ (s)		Tl_2I^+ (120)	Tl_2I^+ (600)		
$Tl_3I_2^+$ (w)		$Tl_3I_2^+$ (1)	$Tl_3I_2^+$ (10)		
		I^+ (5)	TlI_2^+ (8)		
			I^+ (2)		
I^-		I^- (40)	I^- (100)		
TlI_2^- (s)		TlI_2^- (150)	TlI_2^- (400)		

(Continued)

Table IV. (Continued)

TlI	TlI, SF_6	TlI, NO_2	Remove NO_2	Add SF_6	TlI, $TlNO_3$
$Tl_2I_3^-$ (w)		$TlINO_3^-$	$Tl_2I_3^-$ (20)		
		$(TlI)_2NO_3^-$ (10)	NO_3^- (10)		
		NO_3^- (5)			

[a]In experiments performed at 630°K the vapor pressure of TlI was approximately 40μ, while for those performed at 720°K, the vapor pressure was approximately 1 Torr. The number in parenthesis indicates the approximate relative intensity of the ion, uncorrected for any mass discrimination in the spectrometer. Only intensities in a single column should be compared. Where only qualitative intensity measurements were obtained, they are indicated by (s), strong, and (w), weak.

Table V. Ambipolar Diffusion Parameter $C \times 10^{-15}$ (ions/cm sec °K)

Thallium Systems

System	Third Body	Complete Langevin Equation: Tl^+ X^-	$Tl_2^+X^a$ TlX_2^-	Tl_2X^b XlX_2^-	Experimental
TlI	Xe	2.18	1.70	1.62	1.47 ± .1
TlBr	Xe	2.31	1.74	1.67	1.54 ± .1
TlCl	Xe	2.60	1.81	1.74	1.55 ± .1
$TlI-NO_2$	Xe				1.31 ± .1
TlI	Ar	5.06	3.85	3.58	3.63 ± .1
TlBr	Ar	5.27	4.00	3.69	3.75 ± .1
TlCl	Ar	5.72	4.12	3.81	4.12 ± .1
$TlI-NO_2$	Ar				2.63 ± .1

Lead Systems[c]

Ions	Xenon $C_1 \times 10^{-15}$	Xenon $C_2 \times 10^{-15}$	Argon $C_1 \times 10^{-15}$	Argon $C_2 \times 10^{-15}$
PbI^+, I^-	2.05	2.07	4.73	4.86
$Pb_2I_3^+$, I^-	1.62	1.70	3.51	3.75
PbI^+, PbI_3^-	1.56	1.61	3.49	3.67
$Pb_2I_3^+$, PbI_3^-	1.30	1.37	2.78	3.00
Experimental	1.45		3.55	
$PbBr^+$, Br^-	2.20	2.23	4.91	5.03
$Pb_2Br_3^+$, Br^-	1.73	1.83	3.67	3.96
$PbBr^+$, $PbBr_3^-$	1.62	1.68	3.59	3.81
Experimental	2.15		4.80	

(Continued)

Footnotes for Table V

[a]Internuclear distances from neutral molecule.

[b]Internuclear distances from ionic crystals.

[c]The quantities C_1 and C_2 were calculated using the larger and smaller values for the ionic radius of Pb^{2+}, as noted in the text.

Table VI. Critical Collision Radii for Bimolecular Neutralization.

System	ρ(Å)
Tl_2I^+, TlI_2^-	18
Tl_2Br^+, $TlBr_2^-$	21.5
Tl_2Cl^+, $TlBr_2^-$	22
$Tl_2NO_3^+$, $Tl(NO_3)_2^-$	21.5
$Pb_2I_3^+$, I^-	11.7
PbI^+, PbI_3^-	16.1
$PbBr^+$, Br^-	13.8

Table VII. Comparison of Calculated and Experimental Rate Constants.

System	$k_t \times 10^{27}$(calc)	$k_t \times 10^{27}$(expt)
TlI-Xe	20	30
Ar	15	13
TlBr-Xe	15	20
Ar	11	11
TlCl-Xe	15	18
Ar	10	12
$TlNo_3$-Xe	23	19
Ar	20	7
PbI_2-Xe	15	19
Ar	13	9
$PbBr_2$-Xe	16	21
Ar	9	15

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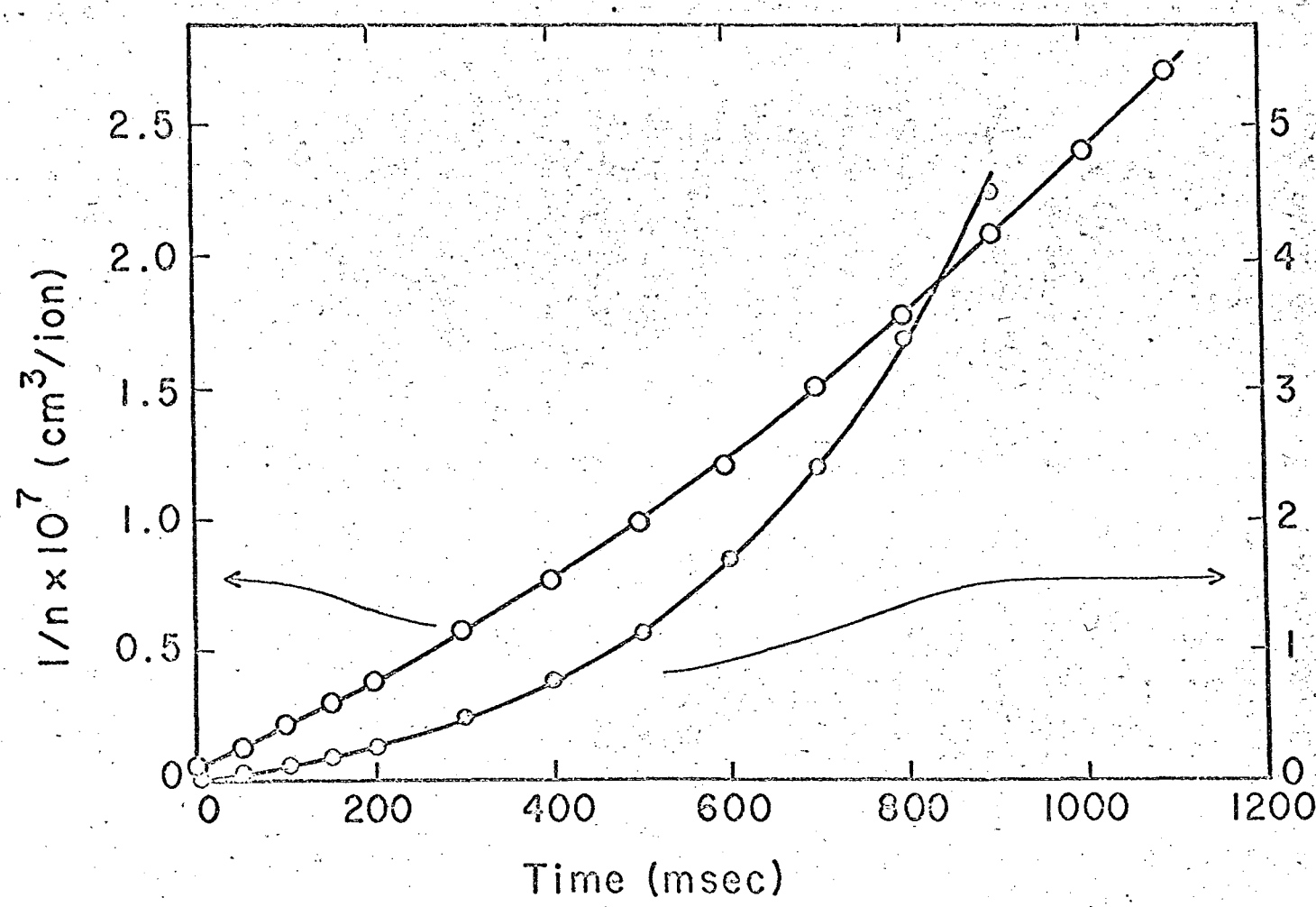

Figure 1. Reciprocal ion concentration as a function of time for the TlI-Xe system. Open circles, 160 Torr Xe; closed circles, 34 Torr Xe. Smooth curves are calculated from the best fit to Eq. (1). Note different ordinates for the different pressures.

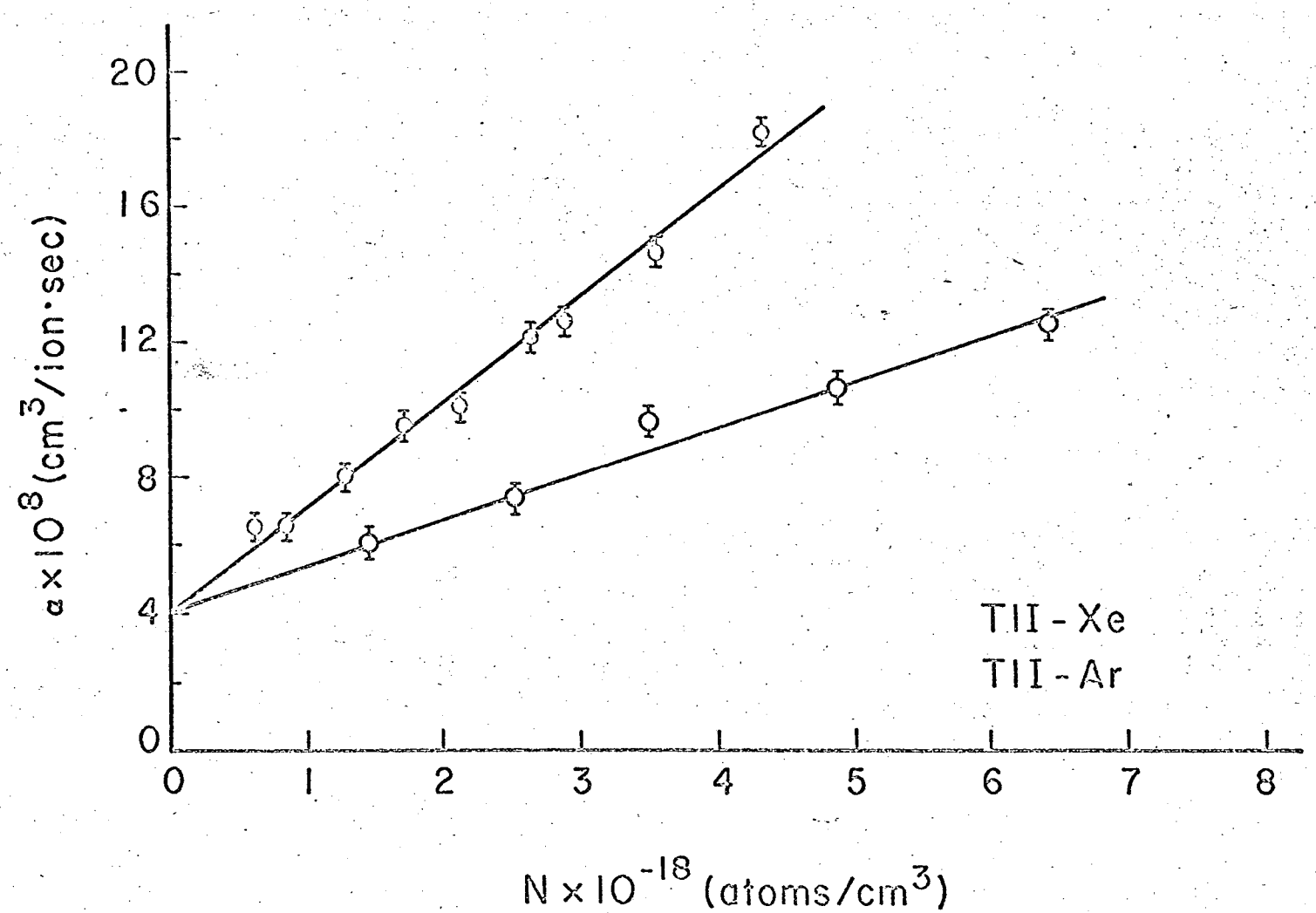

Figure 2. Recombination coefficient α as a function of molecule density. Open circles, TlI-Ar system; closed circles, TlI-Xe system.

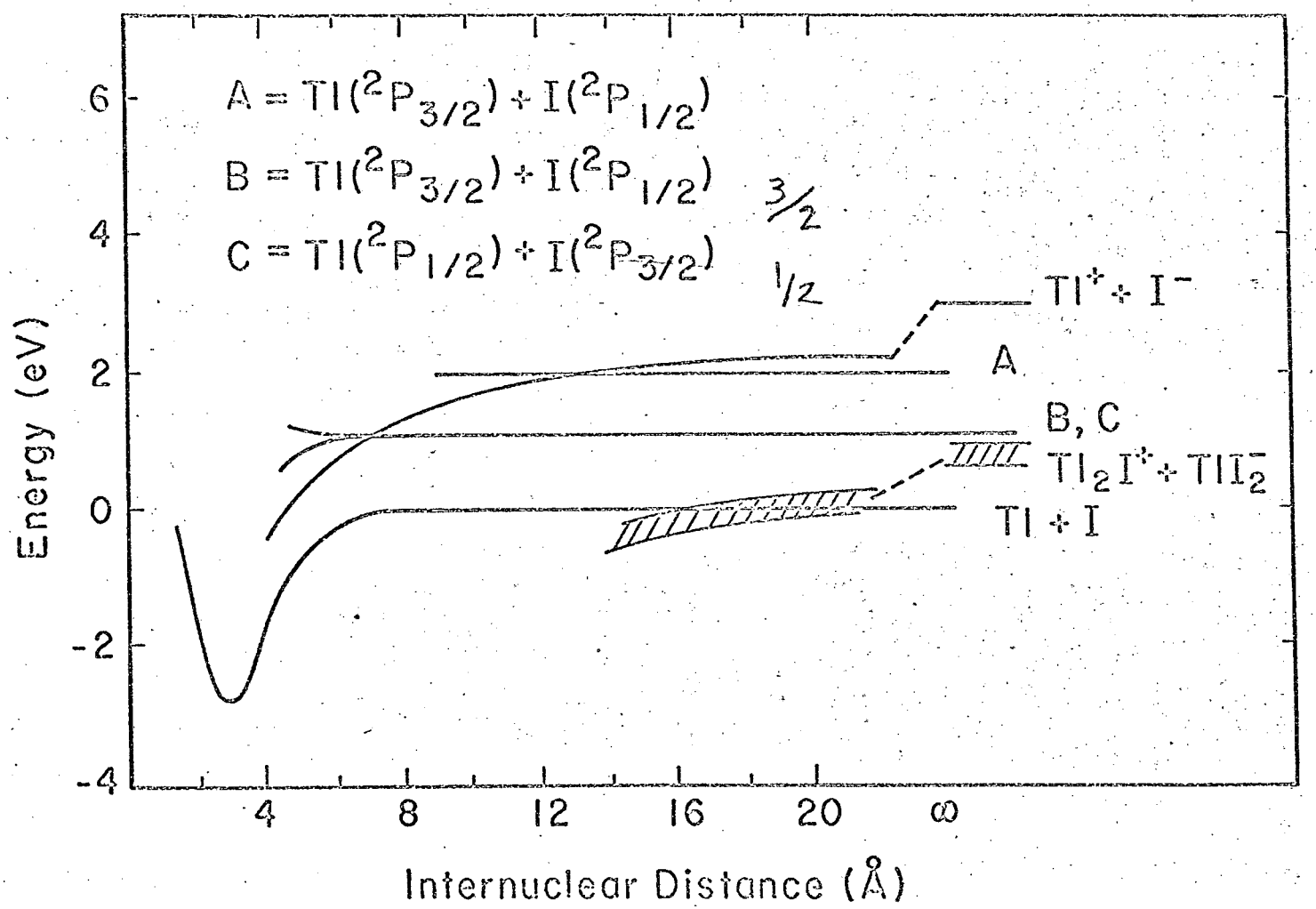

Figure 3. Comparison of potential energy curves for the TlI molecule and the potential energy curve for Tl_2I^+ and TlI_2^-. The uncertainty due to the unknown internal excitation and complexation energy is indicated by shading.

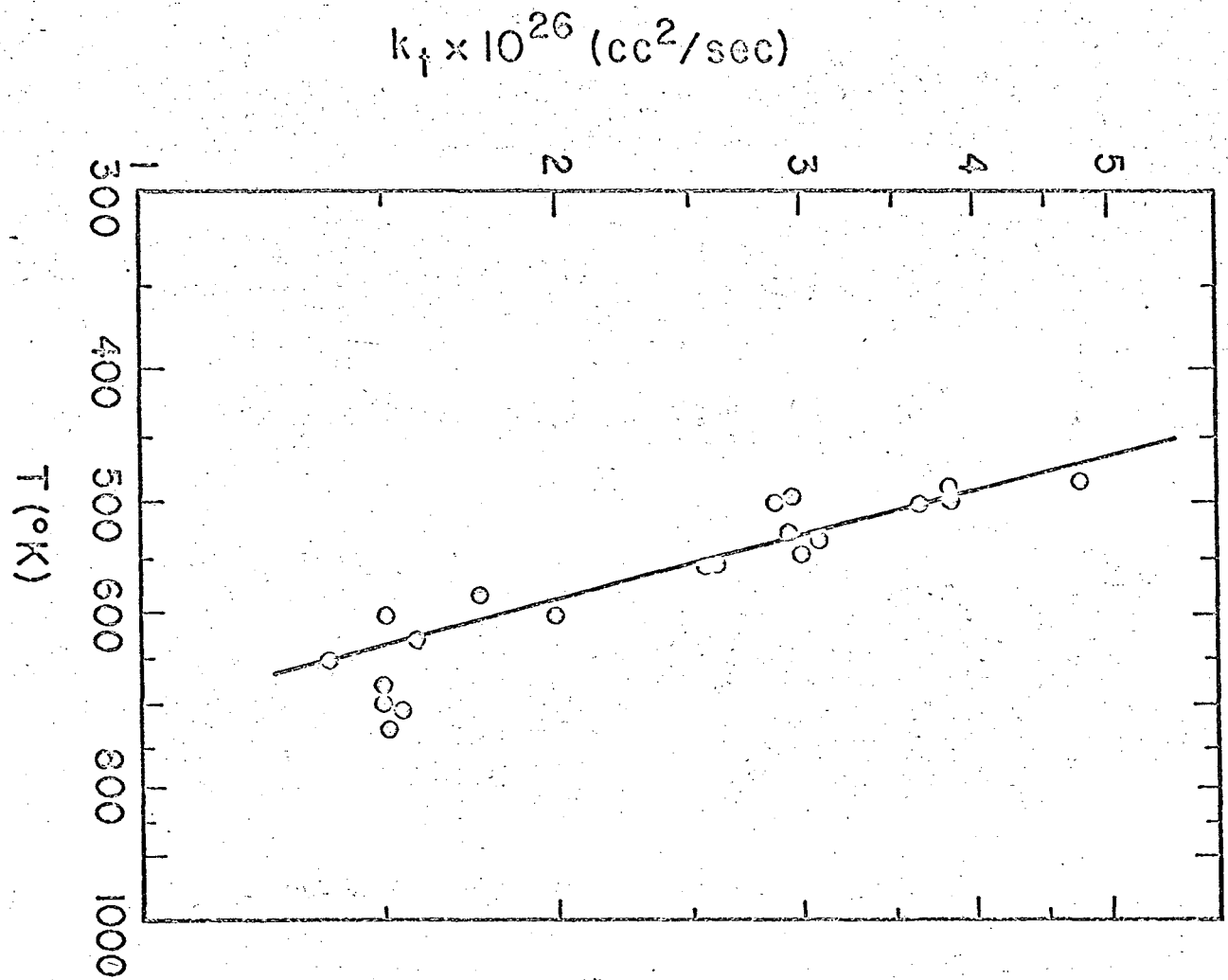

Figure 4. The logarithm of the termolecular rate constant k_t as a function of the logarithm of temperature.

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