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THE CAPTURE RADIUS FOR ION RECOMBINATION

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The Capture Radius for Ion Recombination

by

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An expression for the capture radius defined by Thomson for three-body ion recombination is derived for arbitrary ion and neutral masses. The recombination rate constants calculated from this expression for a variety of systems are compared with the available experimental data. It is found that use of the rigorously calculated capture radius seriously underestimates the recombination rate constant.

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I. INTRODUCTION

Three-body ionic recombination at low pressure is generally believed to take place by the collisional deactivation mechanism originally proposed by J. J. Thomson.[1] The rate determining process is the formation of bound ion pairs from free ions through deactivating collisions with neutral third bodies. At low pressure, this process becomes first order in the inert gas pressure while the ultimate fate of a bound ion pair becomes pressure independent and is determined in a few subsequent ion neutral collisions.[2] The bound ion pair is either redissociated, or further deactivated until the ions approach sufficiently closely for electron transfer to occur. If the rate of formation of bound ion pairs and their redissociation and deactivation are taken into proper account the net neutralization rate can in principle be calculated.

In order to simplify calculations based on the collisional deactivation methanism, Thomson introduced the concept of a capture radius. According to Thomson, recombination of oppositely charged ions occurs if and only if one of the ions undergoes a collision with a neutral when the ions are within a certain distance R_c of each other. The capture radius R_c is generally defined by the condition that the average relative energy of an ion pair after an ion-neutral collision at an ion-ion separation R_c is zero, i.e.,

$$\langle T_{rel} \rangle - \frac{e^2}{R_c} = 0 \qquad (1)$$

where T_{rel} is the relative kinetic energy, and e is the electronic charge. Each ion is assumed to have its thermal average energy at infinite ion-ion separation so that the average in Eq. (1) is over only the directions of the initial velocity vectors and various collision parameters. The rate of recombination is then the number of ions per unit time which undergo collisions with neutrals when the ion-ion separation is less than the capture radius.

Calculations based on a capture radius model have been made by Thomson,[1] Natanson,[3] and Brueckner.[4] In all cases, however, the positive and negative ion masses have been assumed to be equal. A considerable amount of new experimental data[5,6,7] is now available which covers a wide range of ion and neutral masses and provides a more serious test of the capture radius model than has been previously possible. In this paper we generalize the theory to positive and negative ions of different masses and show that the predicted rate constants are considerably too small over a wide range of experimental results.

II. DERIVATION OF THE CAPTURE RADIUS

Consider two ions, 1 and 2, of masses m_1 and m_2, moving initially at large separation with momenta $\underset{\sim}{p}_1^{(0)}$ and $\underset{\sim}{p}_2^{(0)}$ in the laboratory coordinate system (we use the notation of Brueckner[4]). The momenta of the ions at separation r in their center of mass system are

$$\mathfrak{g}_1 = \mathfrak{p}_1 - \frac{m_1}{m_1+m_2}(\mathfrak{p}_1 + \mathfrak{p}_2)$$

and (2)

$$\mathfrak{g}_2 = -\mathfrak{g}_1$$

where

$$\mathfrak{p}_1 = \mathfrak{p}_1^{(0)} + \Delta\mathfrak{g} \tag{3a}$$

and

$$\mathfrak{p}_2 = \mathfrak{p}_2^{(0)} - \Delta\mathfrak{g} \tag{3b}$$

We now consider a collision of ion 1, while at distance r from ion 2, with a neutral third body of mass m_3 and assume the scattering of 1 on 3 is isotropic in the 1-3 center of mass system. The momentum of ion 1 in the 1-3 center of mass system before the collision is

$$\mathfrak{\ell} = \mathfrak{p}_1 - \frac{m_1}{m_1+m_3}(\mathfrak{p}_1+\mathfrak{p}_3)$$

and after the collision

$$\mathfrak{\ell}' = |m_3\mathfrak{p}_1 - m_1\mathfrak{p}_3| \frac{\hat{n}}{m_1+m_3} \tag{4}$$

where $\hat{n}$ is a randomly orientated unit vector. Eq. (4) assumes in addition that "during" the ion-neutral collision the effect of ion 2 on ion 1 can be neglected (it is exact for hard spheres). In the laboratory system the momentum of ion 1 after the collision is

$$\mathfrak{p}_1' = \mathfrak{\ell}' + \frac{m_1}{m_1+m_3}(\mathfrak{p}_1+\mathfrak{p}_3) \tag{5}$$

and in the center of mass system of 1 and 2

$$\underset{\sim}{q}_1' = (m_2\underset{\sim}{p}_1' - m_1\underset{\sim}{p}_2)/(m_1+m_2) \tag{6}$$

The relative kinetic energy is

$$T_{rel} = \frac{q_1^2}{2m_1} + \frac{q_2^2}{2m_2} = \frac{q_1^2}{2\mu} \tag{7}$$

where μ is the reduced mass, $m_1m_2/(m_1+m_2)$. From Eqs. (6) and (7) we have

$$T'_{rel} = \frac{1}{2}\,\mu\left(\frac{\underset{\sim}{p}_1'}{m_1} - \frac{\underset{\sim}{p}_2}{m_2}\right)^2 \tag{8}$$

where T'_{rel} refers to the kinetic energy after the collision with the neutral. Substituting in Eq. (8) from Eqs. (4) and (5) and averaging over the directions of $\hat{n}$ and $\underset{\sim}{p}_3$ gives

$$T'_{rel} = \frac{1}{2}\mu\left\{\frac{m_3^2}{m_1^2(m_1+m_3)^2}\,p_1^2 + \frac{2}{(m_1+m_3)^2}\,p_3^2 + \left[\frac{\underset{\sim}{p}_1}{(m_1+m_3)} - \frac{\underset{\sim}{p}_2}{m_2}\right]^2\right\} \tag{9}$$

From conservation of energy

$$\frac{q_1^{(0)^2}}{2\mu} = \frac{q_1^2}{2\mu} - \frac{e^2}{r} \tag{10}$$

and using Eqs. (2) and (3) we can write Eq. (10) as

$$\frac{\underset{\sim}{p}_2^{(0)}\cdot\underset{\sim}{\Delta q}}{m_2} = \frac{\underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{\Delta q}}{m_1} + \frac{q^2}{2\mu} - \frac{e^2}{r} \tag{11}$$

We now assume that in the laboratory system the ions, at infinite separation, and the third bodies have their thermal average energies, i.e.,

$$\frac{p_1^{(0)2}}{2m_1} = \frac{p_2^{(0)2}}{2m_2} = \frac{p_3^2}{2m_3} = \frac{3}{2}\,kT = T_o \tag{12}$$

Using Eqs. (3), (11), and (12), Eq. (9) becomes, after some manipulation

$$T'_{rel} = T_o - \underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{p}_2^{(0)}\,\frac{\mu}{m_2(m_1+m_3)} + \frac{e^2}{r}\,\frac{m_1(m_1+m_2+m_3)}{(m_1+m_2)(m_1+m_3)}$$

$$+\left(\frac{\underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{\Delta q}}{\mu} + \frac{1}{2}\,\frac{\underset{\sim}{\Delta q}^2}{\mu}\right)\left(1 - \frac{2m_1m_2m_3(m_1+m_2+m_3)}{(m_1+m_2)^2(m_1+m_3)^2} - \frac{m_1(m_1+m_2+m_3)}{(m_1+m_2)(m_1+m_3)}\right) \tag{13}$$

Brueckner[4] assumed $\langle \underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{\Delta q}\rangle = \langle \underset{\sim}{p}_2^{(0)}\cdot\underset{\sim}{\Delta q}\rangle = 0$ where the average is over the directions of $\underset{\sim}{p}_1^{(0)}$ and $\underset{\sim}{p}_2^{(0)}$. With this assumption Eq. (11) becomes

$$\left\langle \frac{\Delta q^2}{2\mu}\right\rangle = \frac{e^2}{r} \tag{14}$$

and for $m_1 = m_2$, Eq. (13) becomes

$$\langle T'_{rel}\rangle = T_o + \frac{e^2}{2r}\left[1 + \frac{m_1^2}{(m_1+m_3)^2}\right]$$

which is Brueckner's result.

In order to eliminate the above assumptions, we need an expression for $\underset{\sim}{\Delta q}$. We first write the relative velocity vector of the two ions, $\underset{\sim}{v}$, in terms of two vectors in the plane of motion, the initial relative velocity vector $\underset{\sim}{v}_{init}$ and the vector $\underset{\sim}{v}_{init} \times \underset{\sim}{M}$, where $\underset{\sim}{M}$ is the angular momentum. Using the equations of motion in parameteric form,[8] we obtain

$$\underset{\sim}{v} = \underset{\sim}{v}_{init}\left\{\mp \frac{1}{r\epsilon^2}\left[(r+a)^2 - a^2\epsilon^2\right]^{\frac{1}{2}} + \frac{\epsilon^2-1}{\epsilon^2}\,\frac{r+a}{r}\right\}$$

$$+ \underset{\sim}{v}_{init} \times \frac{\underset{\sim}{M}}{M}\left\{\mp \frac{\sqrt{\epsilon^2-1}}{r\epsilon^2}\left[(r+a)^2 - a^2\epsilon^2\right]^{\frac{1}{2}} - \frac{\sqrt{\epsilon^2-1}}{\epsilon^2}\,\frac{r+a}{r}\right\} \tag{15}$$

where the lower and upper signs refer to incoming and outgoing particles respectively, ϵ is the orbit eccentricity, and $a = e^2/2E$, where E is the relative energy.

If we write

$$\underset{\sim}{v} = A\,\underset{\sim}{v}_{init} + B\,\underset{\sim}{v}_{init} \times \frac{\underset{\sim}{M}}{M} \tag{16}$$

and use

$$\underset{\sim}{q}_1 = \mu \underset{\sim}{v}$$

then

$$\underset{\sim}{\Delta q} = \mu(A-1)\underset{\sim}{v}_{init} + \mu B\,\underset{\sim}{v}_{init} \times \frac{\underset{\sim}{M}}{M} \tag{17}$$

From Eqs. (15), (16), and (17) we obtain

$$\frac{q^2}{2\mu} = \frac{1}{2}\mu\, v_{init}^2\left[(A-1)^2 + B^2\right]$$

$$= \frac{e^2}{r} - 2E\,(A-1) \tag{18}$$

and

$$\frac{\underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{\Delta q}}{\mu} = (A-1)\,\frac{p^{(0)2}}{m_1} - (A-1)\,\frac{\underset{\sim}{p}_1^{(0)}\cdot\underset{\sim}{p}_2^{(0)}}{m_2} - B\left(\frac{\underset{\sim}{p}_1^{(0)}\times\underset{\sim}{p}_2^{(0)}}{m_2}\cdot\frac{\underset{\sim}{M}}{M}\right) \tag{19}$$

The last term in Eq. (19) depends on the orientation of the plane of motion of the two ions. For given $\underset{\sim}{p}_1^{(0)}$ and $\underset{\sim}{p}_2^{(0)}$, we may average over the azimuthal angle. Since $\langle \underset{\sim}{M} \rangle = 0$, the last term drops out.

Using Eqs. (18) and (19) in Eq. (13), averaging over the directions of $\underset{\sim}{p}_1^{(0)}$ and $\underset{\sim}{p}_2^{(0)}$, and using Eq. (1) to determine the capture radius gives

$$T_o - \frac{e^2}{R_c} \frac{2m_1 m_2 m_3 (m_1+m_2+m_3)}{(m_1+m_2)^2 (m_1+m_3)^2}$$

$$+ \langle A \underset{\sim}{p}_1^{(0)} \cdot \underset{\sim}{p}_2^{(0)} \rangle \frac{m_2 - m_1}{m_2 (m_1+m_2)} \left[1 - \frac{2m_1 m_2 m_3 (m_1+m_2+m_3)}{(m_1+m_2)^2 (m_1+m_3)^2} - \frac{m_1 (m_1+m_2+m_3)}{(m_1+m_2)(m_1+m_3)} \right] = 0 \tag{20}$$

When the positive and negative ions have equal masses, $m_1 = m_2$, and the last term in Eq. (20) is zero. In this case Eq. (20) gives the same result as that obtained by Brueckner[4] although the assumptions made by Brueckner and not strictly valid [compare Eqs. (14) and (18)].

The capture radius is a function of the ion-ion impact parameter through the last term in Eq. (20). The expression $\langle A \underset{\sim}{p}_1^{(0)} \cdot \underset{\sim}{p}_2^{(0)} \rangle$ was evaluated numerically and Eq. (20) was solved for R_c as a function of the impact parameter. The effect of the last term in Eq. (20) is small. Neglecting it changes R_c by approximately 5%. In addition, the change for the incoming ions is opposite to that for the outgoing ions (A is different for the two cases) so that the effect on the recombination rate largely cancels. Neglecting this term yields for collisions

of m_1 with m_3 gives

$$R_c = \frac{e^2}{T_o} \frac{2m_1 m_2 m_3 (m_1+m_2+m_3)}{(m_1+m_2)^2 (m_1+m_3)^2} \tag{21}$$

For collisions of m_2 with m_3, interchange m_1 and m_2. Note that Eq. (21) can be derived from Eq. (13) and the assumptions $\langle \underset{\sim}{p}_1^{(0)} \cdot \underset{\sim}{\Delta q} \rangle = \langle \underset{\sim}{p}_2^{(0)} \cdot \underset{\sim}{\Delta q} \rangle = 0$. It is exact for $m_1 = m_2$.

III. RATE CONSTANT

The three body recombination rate can be written in the form[2]

$$\frac{dn^{\pm}}{dt} = - n^+ n^- 2\pi \int b db d^3 v_1^{(0)} d^3 v_2^{(0)} d^3 v_3 w[\underset{\sim}{v}_1^{(0)}] w[\underset{\sim}{v}_2^{(0)}] w(\underset{\sim}{v}_3) |\underset{\sim}{v}_1^{(0)} - \underset{\sim}{v}_2^{(0)}|$$

$$\times \left\{ \int_{-\infty}^{\infty} dt \frac{|\underset{\sim}{v}_1(t) - \underset{\sim}{v}_3|}{\lambda_1} \eta_1 + \int_{-\infty}^{\infty} dt \frac{|\underset{\sim}{v}_2(t) - \underset{\sim}{v}_3|}{\lambda_2} \eta_2 \right\} \tag{22}$$

where b is the ion-ion impact parameter, n^+ and n^- the positive and negative ion densities respectively, and $w(\underset{\sim}{v})$ is the Maxwell distribution. The factor $n^- 2\pi b db |\underset{\sim}{v}_2^{(0)} - \underset{\sim}{v}_1^{(0)}|$ is the flux of negative ions incident, with impact parameter b, on a single positive ion. The two factors in brackets represent the probability that either a negative or a positive ion will undergo a collision with the neutral third body in such a way as to bind the ions stably.

With λ_1 the mean free path of ion 1, $|\underset{\sim}{v}_1 - \underset{\sim}{v}_3|/\lambda_1$ is the probability per unit time that an ion of volicity $\underset{\sim}{v}_1$ collides

with a neutral of velocity $\underset{\sim}{v}_3$. If $\eta_1(\underset{\sim}{v},\underset{\sim}{v}_2,\underset{\sim}{v}_3,b,t)$ is the probability that for given values of the arguments the collision of 1 and 3 lead to a bound ion pair, then

$$\int d^3v_3\ w(\underset{\sim}{v}_3) \int_{-\infty}^{\infty} dt\ \frac{|\underset{\sim}{v}_1(t)-\underset{\sim}{v}_3|}{\lambda_1}\ \eta_1 \tag{23}$$

represents the probability that the ion-ion encounter at impact parameter b leads to a recombination through collisions of ion 1 with the neutral.

The recombination coefficient obtained from Eq. (22) is

$$\alpha = 2\pi \int b\,db\,d^3v_1^{(0)}d^3v_2^{(0)}d^3v_3 w[\underset{\sim}{v}_1^{(0)}]w[\underset{\sim}{v}_2^{(0)}]w(\underset{\sim}{v}_3)|v_1^{(0)}-v_2^{(0)}|\times$$
$$\left\{\int_{-\infty}^{\infty} dt\ \frac{|\underset{\sim}{v}_1(t)-\underset{\sim}{v}_3|}{\lambda_1}\ \eta_1 + \int_{-\infty}^{\infty} dt\ \frac{|\underset{\sim}{v}_2(t)-\underset{\sim}{v}_3|}{\lambda_2}\ \eta_2\right\} \tag{24}$$

For the capture radius model we have

$$\eta_1 = \begin{cases} 1 & r < R_1 \\ 0 & r > R_1 \end{cases}$$
$$\eta_2 = \begin{cases} 1 & r < R_2 \\ 0 & r \geq R_2 \end{cases} \tag{25}$$

where R_1 and R_2 are the respective capture radii for collisions of ions 1 and 2 with the neutral.

The mean free path λ, equals $1/N\sigma$ where N is the neutral number density and σ is the ion-neutral cross section. Besides the "hard sphere" interaction, ions and neutrals exhibit charge-induced dipole attractive forces. In order to take these forces into account we use the cross section corresponding to

orbiting of the ion and neutral, i.e.,

$$\sigma_{13}^{orb} = \pi b_o^2 = 2\pi \left(\frac{\alpha_{pol} e^2}{\mu_{13}} \right)^{\frac{1}{2}} \frac{1}{v_{13}} \tag{26}$$

where α_{pol} is the polarizability of the neutral, μ_{13} the 1,3 reduced mass, v_{13} the 1,3 relative velocity and b_o the ion-neutral orbiting impact parameter. For $b > b_o$, the scattering angle rapidly approaches zero, consequently the deactivation of ions from collisions with ion-neutral impact parameter larger than b_o is small. The orbiting cross section is also approximately isotropic, an assumption made in deriving the capture radius.

The orbiting cross section should be used in Eq. (23) only when it is larger than the "hard sphere" cross section ($\sigma^{h.s.}$). For the systems considered in this paper (see Table I) $\sigma^{orb} > \sigma^{h.s.}$ for the free ions. However, since $\sigma^{orb} \propto 1/v_{13}$, σ^{orb} decreases as the ions approach and generally both cross sections are needed in Eq. (23). For the data reported in Table I, however, σ^{orb} and $\sigma^{h.s.}$ generally become equal at a sufficiently small ion-ion separation, compared to the capture radius, that the effect of $\sigma^{h.s.}$ is small ($\sigma^{h.s.}$ represents an average "hard sphere" cross section for the case of complex ions). For all calculations reported in Table I σ^{orb} was used in Eq. (23) at all ion-ion separations. For the experiments done at room temperature, the capture radius is large enough (100-200 Å) that the effect of $\sigma^{h.s.}$ is negligible. For the

high temperature experiments, the capture radii as well as the orbiting cross sections are smaller and $\sigma^{h.s.}$ becomes more important. In the high temperature Xe studies, the worst case occurs for collisions of TlI_2^- with Xe where the ion-ion separation at which $\sigma^{orb} = \sigma^{h.s.}$ is 22.7 Å while the capture radius is 44.4 Å. Thus, in approximately 25% of the cross sectional area we use a somewhat smaller ion-neutral cross section than is valid. In the case of the high temperature Ar experiments, the calculated rates may be as much as 50% too low.

Using Eqs. (25) and (26) and the orbit equations of the ions,[8] integration of Eq. (23) gives

$$\int d^3v_3 w(\underset{\sim}{v}_3) \int_{-\infty}^{\infty} dt \, \frac{|\underset{\sim}{v}_1(t)-\underset{\sim}{v}_3|}{\lambda_1} \eta_1 = N2\pi \left(\frac{\alpha_{pol} e^2}{\mu_{13}}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dt \, \eta_1$$

$$= N4\pi \left(\frac{\alpha_{pol} \, e^2}{\mu_{13} v_{init}^2}\right)^{\frac{1}{2}} \left[\sqrt{R_1^2+2R_1 a-b^2} - a \cosh^{-1} \frac{R_1+a}{\sqrt{a^2+b^2}}\right] \qquad (27)$$

where $a = e^2/2E$.

Integration over b from $b = 0$ to $b = b_{max} = (R^2+e^2R/E)^{\frac{1}{2}}$, (R is the capture radius) gives

$$\alpha = \int d^3v_1^{(0)} d^3v_2^{(0)} w[\underset{\sim}{v}_1^{(0)}] w[\underset{\sim}{v}_2^{(0)}] \alpha'(E)$$

$$= \int_z^{\infty} dE w(E) \, \alpha'(E) \qquad (28)$$

where $\alpha'(E) = 8\pi^2 N \times$

$$\left\langle \left(\frac{\alpha_{pol} e^2}{\mu_{13}}\right)^{\frac{1}{2}} \left\{ \frac{(R_1^2+2R_1 a)^{3/2}}{3} - \frac{a^2(R_1+a)}{2}\left[\sqrt{\left(\frac{R_1+a}{a}\right)^2 - 1} - \left(\frac{a}{R_1+a}\right)\cosh^{-1}\left(\frac{R_1+a}{a}\right)\right]\right\} \right.$$

$$\left. + \left(\frac{\alpha_{pol} e^2}{\mu_{23}}\right)^{\frac{1}{2}} \left\{ \frac{(R_2^2+2R_2 a)^{3/2}}{3} - \frac{a^2(R_2+a)}{2}\left[\sqrt{\left(\frac{R_2+a}{a}\right)^2 - 1} - \left(\frac{a}{R_2+a}\right)\cos^{-1}\left(\frac{R_2+a}{a}\right)\right]\right\} \right\rangle$$

and $w(E)$ is the Maxwell distribution for the relative energy.

As $z \to 0$, the integral in Eq. (28) diverges. This is due to the fact that as $E \to 0$, the capture probability in Eq. (27) approaches a constant, $b_{max} \to \infty$ and the capture cross section approaches infinity. The formulation presented here, however, is valid only if $b \lesssim \lambda$. For $b > \lambda$, proper account must be taken of multiple ion-neutral collisions.

The mean free path at the densities of interest here (3×10^{17} - 3×10^{18} cm^{-3}) is large enough ($\sim 10^{-4}$ cm) that the Coulomb energy at an ion-ion separation of approximately one mean free path is small compared to kT. Thus the distribution of relative energies at this separation is approximately Maxwellian and the effect of multiple collisions is simply to rerandomize impact parameters such that in Eq. (24) one need not consider impact parameters larger than approximately one mean free path.

At $E = E_o = e^2R/(\lambda^2-R^2)$, $b_{max} = \lambda$. By using the low energy limit of Eq. (27) and $b_{max} = \lambda$, it is easy to show that the contribution to the recombination rate from energies less than E_o is negligible. Although α/N now depends on the neutral number

density through E_o, numerical calculations show that it varies by less than 1% over the density range considered here.

The calculated values given in Table I are obtained from a numerical integration of Eq. (28). The results are given for $N = 3 \times 10^{18}$ cm^{-3}.

The formula

$$\alpha = 1.33\ \alpha'\ (3/2\ kT)$$

is valid in all cases to within 2%. It is easy to show that $\alpha \propto T^{-3}$ to within the same approximation.

IV. RESULTS

In Table I some experimental three body rate constants are given along with values calculated from Eq. (29). In the calculations the polarizabilities of Xe, Kr, Ar, and O_2 are taken to be 4.01, 2.48, 1.60, and 1.0 $Å^3$, respectively. The calculated values are seen to be consistently well below the experimental values. In addition, the calculated relative rate constants for a given neutral and different ion pairs, or for a given ion pair and different neutrals are, in general, not in accord with experiment.

The capture radius that is used in these calculations [defined by Eq. (1)] has been critized by Brueckner[4] on the grounds that not all "captured" ions are stable against further ion-neutral collisions. If additional restrictions are imposed, the capture radius is lowered considerably and the calculated rate is lowered still further.

For the O_2^+, O_2^-, O_2 system, Feibelman[2] has obtained the three body rate by numerical methods. In his paper he avoided the use of a capture radius and by the Monte Carlo method took

proper account of averages of direction, velocity, and collision parameters. He found that by considering the effects of dissociative collisions and by taking averages correctly, the rate constant turns out an order of magnitude larger than calculations based on a capture radius and is in good agreement with experiment.

These results imply that the collisional deactivation mechanism is probably an adequate description of three body recombination, however, calculations based on a rigorously applied capture radius model will generally be considerably in error. It has been shown recently,[7] however, that if the capture radius originally adopted by Thomson is used and some simplifying assumptions are made with regard to the ion-neutral collision frequency, the resulting formula predicts rate constants which are in quite good agreement with experiment. While the formulation has little theoretical rigor, it is quite useful for predicting three body rates.

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Table I

T(°K)	System	Neutral	$\alpha/N \times 10^{26}$ (cm^6/sec)	
			Exper.	Calc.
298	O_2^+, O_2^-	O_2	12.2[a]	3.94
298	NO^+, NO_2^-	Xe	27.8[b]	10.01
298	NO^+, NO_2^-	Kr	17.5[b]	7.67
298	NO^+, NO_2^-	Ar	14.5[b]	5.10
530	Tl_2^+I, TlI_2^-	Xe	3.04[c]	0.00936
530	Tl_2^+I, TlI_2^-	Ar	1.30[c]	0.00980
590	Tl_2^+Br, $TlBr_2^-$	Xe	1.96[c]	0.104
590	Tl_2^+Br, $TlBr_2^-$	Ar	1.06[c]	0.0111
610	Tl_2^+Cl, $TlCl_2$	Xe	1.76[c]	0.150
610	Tl_2^+Cl, $TlCl_2^-$	Ar	1.18[c]	0.0193
707	$PbBr^+$, Br^-	Xe	2.06[c]	0.361
707	$PbBr^+$, Br^-	Ar	1.53[c]	0.157

a. Reference 5.

b. Reference 6.

c. Reference 7.

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