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Berkeley, California

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Gaseous Ion Recombination Rates. II

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Abstract

An analysis of the mechanics of three body ion recombination is given. The relative efficiencies of various gases in promoting ion recombination are calculated and found to be in satisfactory agreement with experiment. The calculations lead to qualitative conclusions about how mass, relative velocity, and the nature of the deactivation criterion affect the magnitude of the recombination rate.

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In an earlier publication[1] we presented experimental evidence that suggested that three body recombination of gaseous ions proceeds by the following mechanism:

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

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

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

The species $(A^+B^-)^*$ is a pair of ions in an unbound orbit about each other, but in a condition such that if one of them collides with a neutral molecule M, a bound ion pair in an elliptical orbit will be formed. The most probable fate of this bound ion pair is charge transfer followed by dissociation to neutral fragments. If neither member of the unbound pair $(A^+B^-)^*$ undergoes a collision, the two ions separate via their hyperbolic orbit. A steady state treatment of the mechanism gives

$$-\frac{d[n]}{dt} = \frac{k_1 k_3 [A^+][B^-][M]}{k_2 + k_3[M]} \equiv \alpha_t [A^+][B^-]$$

where α_t is the ion recombination coefficient that refers to this three body process only.

The above mechanism is essentially a restatement of the process proposed by Thomson[2] for three body ion recombination. Thomson developed an expression for α_t using a simplified description of the mechanics of the three body collision. He first assumed that although two ions in proximity would have

abnormally large kinetic energies due to the action of the Coulomb force, a collision of one of these ions with a neutral molecule would restore the ion kinetic energy to the average value characteristic of thermal equilibrium, 3/2 kT. This suggested that if either of two ions undergoes a collision while the two ions are closer than a distance d defined by $e^2/d = 3/2\ kT$, a bound ion pair and, eventually, neutral fragments will result. Thomson calculated this collisional deactivation rate under the assumption that the ions travel past each other on straight lines and at constant speed. The frequency of deactivating collisions was related to the ionic mean free path, as derived from diffusion or mobility measurements.

After considering these severe simplifications, it is not surprising that the ability of the Thomson theory to predict absolute values of α_t or even relative values for different inert gases is somewhat limited. In particular, the assumption that the ion kinetic energy is restored to 3/2 kT after a collision must fail badly if the masses of the ion and neutral differ greatly. Also, the definition of a collision in terms of a mean free path derived from transport data may cause difficulty. That is, the collisional deflection angles that are most important in determining, let us say, ion mobility may not be those most effective in reducing the kinetic energy of one ion relative to another moving ion. Finally, the magnitude and direction of the ion velocities do change as the ions approach each other, and thus the probability that a given angular deflection will result in deactivation may be a function

of ion separation. None of these objections has been eliminated in the various refinements of the Thomson theory which have been made. The purpose of this paper is to present the details and application of an analysis of the ion recombination problem which, while retaining the spirit of the Thomson treatment, features the partial elimination of its simplifying assumptions.

Collisional Mechanics

Our fundamental problem is to find the rate at which a pair of unbound ions in an otherwise arbitrary mechanical condition will undergo collisional deactivation to a bound state. This rate, together with the probability of finding a pair of ions in an arbitrary state, allows calculation of the three body recombination coefficient α_t.

We consider a pair of ions of opposite charge (particles 1 and 2) and a neutral molecule (particle 3). The ions are initially in a hyperbolic orbit when one of them (particle 1) undergoes a collision with the neutral molecule. The time of the ion-neutral interaction is presumed to be so short that the ion-ion distance does not change during the ion-neutral collision. This approximation would be exact if there was only a hard sphere force law between the ion and neutral. Together with the assumption that the neutral interacts with only one of the ions, this simplification breaks the general three-body problem into a pair of two-body problems. Both assumptions are partially justified by the fact that the Coulomb force has a much greater range than does the ion-induced

dipole-hard sphere core force we assume acts between the ion and neutral, and by the fact that our experimental data[1] suggest that most deactivations occur when the ions are greatly separated. There is probably no other recombination problem in which these particular assumptions are so well justified.

In the subsequent calculation we assume that all collisions are elastic, and all intermolecular potentials are spherically symmetric. In addition, we neglect processes in which ions are deactivated by multiple collisions with neutrals. This latter assumption is valid at low pressures, but almost certainly breaks down at pressures near 1 atm.

The condition for the ion pair to be bound is that the total energy of relative motion and position be negative, when the zero of potential energy is taken at infinite ion separation. If $T_R(\infty)$ and $T_R(\rho)$ are the relative kinetic energies at infinite separation and at $r_{12} = \rho$, then for two ions that have been undisturbed

$$T_R(\rho) = T_R(\infty) + \frac{e^2}{\rho}$$

If particle 1 undergoes a collision with a neutral while the two ions are separated by a distance ρ, the minimum criterion for producing a bound ion pair is that the decrease in the relative kinetic energy of the ions ΔT_R must be greater than $T_R(\infty)$. That is

$$\Delta T_R \equiv \frac{\mu_{12}}{2} (g_{12}^2 - g_{12}'^2) \geq T_R(\infty) \qquad (1)$$

where μ_{12} is the reduced mass of the ion pair, and g_{12} and g'_{12} are the magnitudes of the relative velocity before and after the ion-neutral collision respectively.

Let the velocities of the ions in a laboratory coordinate system immediately before the ion-neutral collision be $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_2$, and immediately after the collision be $\underset{\sim}{v}'_1$ and $\underset{\sim}{v}'_2 = \underset{\sim}{v}_2$. The constancy of $\underset{\sim}{v}_2$ results from our assumptions that the ion-neutral collision is instantaneous and that the neutral interacts only with ion 1. If the angle between $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_2$ is γ, and between $\underset{\sim}{v}'_1$ and $\underset{\sim}{v}_2$ is γ', then

$$g_{12}^2 = v_1^2 + v_2^2 - 2v_1v_2 \cos\gamma$$

and a similar equation can be written involving g'_{12}, v'_2, v_2, and γ'. Using these relations in Eq. (1) gives

$$\Delta T_R = \frac{\mu_{12}}{2} [v_1^2 - v_1'^2 + 2v_2(v'_1 \cos\gamma' - v_1 \cos\gamma)] \qquad (2)$$

This equation shows that if particle 2 is moving, then not only the change in the magnitude of the velocity of ion 1, but also the angle through which v_1 is deflected is important in deciding whether deactivation takes place. Thus it is conceivable that a massive neutral can deactivate a very light ion by deflecting it correctly, even though in such a collision the magnitude of the ion velocity cannot change very much. One such type of deflection is one in which $\gamma = \pi$ and $\gamma' = 0$, for then the ions first approach or recede from each other and then travel in the same direction. For such a case Eq. (2) shows

that the ions could become bound even if $v_1 = v_1'$. On the other hand, if a massive ion were to collide with a very light neutral, then the ion would neither be deflected nor slowed very much, so that ΔT_R would necessarily be small. Thus, if deactivation efficiency of a neutral is related to the size of the ΔT_R it can induce, we would expect light neutrals to be poor deactivators for heavy ions, but heavy neutrals might have relatively high efficiency with both light and heavy ions.

For the calculation we performed, it was convenient to express the deactivation requirement in terms of $\Delta T_1 = (m_1/2)(v_1^2 - v_1'^2)$ and $\cos\gamma$. From Eqs. (1) and (2) we get

$$\left(1 - \frac{\Delta T_1}{T_1}\right)^{1/2} \cos\gamma' \geq \frac{T_R(\infty) - \Delta T_1(\mu_{12}/m_1)}{\mu_{12} v_1 v_2} + \cos\gamma \qquad (3)$$

after having made the substitution

$$(1 - \Delta T_1/T_1)^{1/2} = v_1'/v_1$$

Eq. (3) implicitly states the minimum requirement for producing a bound pair, for a given γ, T_1 and $T_R(\infty)$. Thus by calculating ΔT_1 and γ' we can ascertain whether a given ion-neutral collision causes deactivation of an ion pair in a particular initial state.

Now we must examine the collision between the ion and neutral in detail. Figure 1 is a vector diagram for the ion-neutral collision in which the initial velocity vectors $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_3$, both measured in the laboratory coordinate system, have been drawn from a common origin. These two vectors define a

plane which contains the initial ion-neutral relative velocity vector $\underset{\sim}{g}_{13}$, and the corresponding center of mass velocity vector $\underset{\sim}{V}_{13}$. The final relative velocity vector is $\underset{\sim}{g}'_{13}$, and the final velocity vectors in the laboratory system are $\underset{\sim}{v}'_1$ and $\underset{\sim}{v}'_3$. The tip of the center of mass vector divides the relative velocity vector in two segments whose lengths are in the ratio m_1/m_3. The effect of the ion-neutral collision is to rotate the relative velocity vector by an angle χ_{13} about the tip of the center of mass vector, while leaving the magnitude of g_{13} unchanged. In contrast, the ion velocity $\underset{\sim}{v}_1$ as seen in the laboratory system changes in magnitude and in direction.

Now χ_{13} can be determined by integration of the expression

$$\chi = \pi - 2b \int_{r_m}^{\infty} \frac{dr/r^2}{[1-2\Phi(r)/\mu g^2 - b^2/r^2]^{1/2}} \qquad (4)$$

where in the present case b would be the ion-neutral impact parameter, μ and Φ the corresponding reduced mass and potential energy, g the initial relative speed, and r_m is the distance of closest approach.

The ion-neutral potential energy was assumed to be

$$\Phi_{13} = -\frac{\alpha' e^2}{2r_{13}^4} \qquad r_{13} > s$$

$$\Phi_{13} = \infty \qquad r_{13} \leq s$$

where α' is the polarizability of the neutral, e is the electronic charge, and s is a hard sphere radius defined by

$s = (s_1+s_3)/2$, where s_1 and s_3 are hard sphere radii for the ion and neutral respectively. Table I gives the values of s used in our calculation. Goldschmidt's values[3] for the distance between ionic and molecular centers upon impact were used as lower limits, and Lennard-Jones σ values[4] as upper limits. The angles χ_{13} were found from Hassé's expressions[5] for Eq. (4).

Now we must express ΔT_1 and $\cos\gamma'$ in terms of the states of the ions and the deflection angle χ_{13}. After substituting the relations

$$\underset{\sim}{v}_1 = \underset{\sim}{V}_{13} + \underset{\sim}{g}_{13} \frac{m_3}{m_1+m_3}$$

$$\underset{\sim}{v}_1' = \underset{\sim}{V}_{13} + \underset{\sim}{g}_{13}' \frac{m_3}{m_1+m_3}$$

into the definition of ΔT_1, we find

$$\Delta T_1 = \mu_{13}\underset{\sim}{V}_{13}\cdot(\underset{\sim}{g}_{13} - \underset{\sim}{g}_{13}') \qquad (5)$$

This equation shows that the magnitude of ΔT_1 depends on the coordinate system from which the ion-neutral collision is observed. In particular, if the observing system should be moving with the center of mass of the ion-neutral system, then $V_{13} = 0$, and no energy change would be apparent. Further reduction of Eq. (5) gives

$$\Delta T_1 = \mu_{13}V_{13}g_{13}[\cos\eta(1-\cos\chi_{13}) + \sin\eta \sin\chi_{13}] \qquad (6)$$

This equation allows calculation of ΔT_1 in terms of the initial parameters of the ion-neutral collision, since through Eq. (4)

χ_{13} can be found, and from the geometry of Fig. 1 we find $\cos\eta$ is given by

$$\cos\eta = \frac{1}{2X}\left(\frac{m_1^2 v_1^2}{\mu_{13}^2 g_{13}^2} - X^2 - 1\right) \tag{7}$$

$$X = \frac{V_{13}}{g_{13}}\left(\frac{m_1+m_3}{m_3}\right)$$

It only remains to find γ' from the initial conditions. To do this we must consider Fig. 2, a vector diagram for the ion-ion system. As Fig. 2 shows, γ' depends not only on β, the angle through which v_1 is rotated, but on φ, the angle between the plane of $\underset{\sim}{v}_1'$ and $\underset{\sim}{v}_2$ and that of $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_1'$. From the geometry of Fig. 2 we obtain

$$\cos\gamma' = \cos\beta \cos\gamma + \sin\beta \sin\gamma \cos\varphi.$$

To use this expression we must have β in terms of quantities derivable from the initial conditions. The geometry of Fig. 1 gives us

$$\tan(\beta+\theta) = \frac{\sin(\chi_{13} + \eta)}{X + \cos(\chi_{13}+\eta)} \tag{8}$$

$$\tan\theta = \frac{\sin\eta}{X + \cos\eta} \tag{9}$$

Eqs. (4) through (9) permit us to calculate ΔT_1 and γ' for any set of initial ion-neutral conditions, and thus to decide whether a given collision will cause deactivation for a particular set of ion velocities $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_2$.

Weighting of Collision Parameters

In this section we will describe how the values of the collision parameters were weighted in the calculation of $k_3(\rho)$ the deactivation rate constant for two ions separated by a distance ρ. To simplify the problem, we took the kinetic energy of each of the three particles to be equal to 3/2 kT at infinite separation. This set the magnitudes of the velocity vectors in the laboratory system, and avoided an explicit average over the Maxwell-Boltzmann speed distribution. However, since the masses of the three particles were generally different, their speeds were different, and since the angles between the velocity vectors were allowed to vary over their appropriate ranges, a variety of relative velocities were included in the calculation.

We consider now a particular ion-neutral deflection angle χ_{13}. For a given ρ, $\underset{\sim}{v}_1$, and $\underset{\sim}{v}_2$ it is possible to decide what range of values of φ will lead to deactivation. Since φ is uniformly distributed, the fraction of collisions with deflection angles χ_{13} which produces deactivation is $\Delta\varphi/2\pi$, where $\Delta\varphi$ is the range of φ which produces deactivation. The rates at which collisions occur to give the various values of χ_{13} must be multiplied by these angular "steric factors."

For a given ion-neutral relative speed, χ_{13} is a function only of the ion-neutral impact parameter. Thus, if we weight each value of χ_{13} with the probability of its occurrence, this is equivalent to averaging the deactivation rate over the ion-neutral impact parameter. To accomplish this, we divided the

range of $|\chi_{13}|$ into 6 regions, and calculated the rate at which deflection angles in each region were formed. The details of this calculation are in the Appendix. In particular, we calculated the rate of formation of a range of deflection angles $\Delta|(\chi_{13}-m2\pi)|$, where m is a positive integer that insures that $-\pi \leq \chi_{13} - m2\pi \leq \pi$. The calculation of a range of absolute values of the deflection angle is necessary because for a given impact parameter a positive or negative deflection angle can be obtained.

The rate of formation of a particular range $\Delta\chi_{13}$ at χ_{13} is

$$\frac{d(\Delta\chi_{13})}{dt} = \pi\Delta(b_{13}^2 g_{13})[M][Ion]$$

where $\pi\Delta(b_{13}^2 g_{13})$ is the partial rate constant for the desired range of angles at χ_{13}. The rate of formation of angles in the larger region $\Delta|(\chi_{13} - m2\pi)|$ is the sum of such partial rates for all different values of $b_{13}^2 g_{13}$ which give deflections in the desired range.

To use these weighting factors we calculated the fraction of collisions with $+\chi_{13}$ which gives deactivation, averaged this with the same quantity for $-\chi_{13}$, and multiplied this average by the rate of formation of χ_{13} in the range $\Delta(|\chi_{13} - m2\pi|)$. This was repeated until the range of χ_{13} from 2° to 180° was covered. The calculations were cut off at $\chi_{13} = 2°$ to avoid the infinity in the cross section which occurs as χ_{13} goes to zero. The results of the calculation show that deflections of 20° or less are likely to cause deactivation only when the value of ρ is small, and the probability of such situations diminishes as ρ becomes smaller.

To this point, the procedure constitutes an average over the impact parameter b_{13}, and the inclination of the ion-neutral orbital plane. Thus we have the deactivation rate for ions separated by a distance ρ, when the particle velocities are $\underset{\sim}{v}_1$, $\underset{\sim}{v}_2$ and $\underset{\sim}{v}_3$. This deactivation rate must be averaged over the values of $\underset{\sim}{v}_3$. Since we chose $\underset{\sim}{v}_3$ to have a fixed magnitude, we performed the average by assuming that all angles ν between $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_3$ were equally probable at infinite ion-neutral separation.

Next we performed a partial average over $\underset{\sim}{v}_1(\rho)$ and $\underset{\sim}{v}_2(\rho)$. For a given set of masses, we can regard these vectors as being determined by the kinetic energy of the motion of the centroid of the ion pair, the corresponding kinetic energy of relative motion, and the angle ϵ between $\underset{\sim}{g}_{12}$ and $\underset{\sim}{V}_{12}$, as shown in Fig. 2. The rate of deactivation must be calculated for each ϵ and then the results weighted by the probability of having ϵ in the region $\Delta\epsilon$ about ϵ. However, the angles ϵ are not uniformly distributed. The difference $\delta\epsilon$ between $\epsilon(\rho)$ and $\epsilon(\infty)$ is just the angle through which the ion-ion collision has rotated the relative velocity vector about the center of mass vector. Thus, even for a fixed value of $g_{12}(\infty)$ the angle $\epsilon(\rho)$ will depend on the impact parameter b_{12}. The values of $\epsilon(\rho)$ must be properly weighted considering the values of b_{12} which produce them.

At $r_{12} = \infty$, $\delta\epsilon = 0$ or $\delta\epsilon = \chi_{12}$, where χ_{12} is the asymptotic value of the ion-ion deflection angle, and the first value applied to the start of the ion-ion collision, and the second to the

finish of the collision. Intermediate values of $\epsilon(\rho)$ can be computed from

$$\epsilon(\rho) = \epsilon(\infty) \pm (\delta_o - \delta) \qquad \text{incoming leg}$$

$$\epsilon(\rho) = \epsilon(\infty) \pm (\delta_o + \delta) \qquad \text{outgoing leg}$$

where

$$\tan \delta_o = 1/(e_c^2-1)^{1/2}$$

$$\tan \delta = \tanh \xi/(e_c^2-1)^{1/2}$$

The quantity e_c is the eccentricity of the orbit, given by

$$e_c = \left(1 + \frac{\mu_{12}^2 g_{12}^4 b_{12}^2}{e^4}\right)^{1/2}$$

and e is the electronic charge. The parameter ξ is related to r_{12} by

$$r_{12} = \frac{e^2}{\mu_{12} g_{12}^2} (e_c \cosh \xi - 1)$$

The quantities $\tan \delta$ and $\tan \delta_o$ are the slopes of lines perpendicular to the hyperbolic orbit at $r_{12} = \rho$ and at $r_{12} = \infty$ respectively. The choice of sign for $(\delta_o - \delta)$ results from the fact that the ion-ion collision may increase or decrease ϵ.

To calculate the weighting factors for the $\Delta\epsilon$ regions we found the distribution of ϵ corresponding to equal values of Δb_{12}^2 from $b_{12}^2 = 0$ to $b_{12}^2 = b_m^2$, where b_m is the maximum impact parameter which gives ρ as the distance of closest approach. This distribution was then used to calculate the weighting factor for an ion-ion collision in which ϵ was in a particular $\Delta\epsilon$ region, and a sum over all accessible values of ϵ was taken.

Thus, an average over $\epsilon(\rho)$ amounts to an average over the allowed values of the ion-ion impact parameter for a fixed value of g_{12}.

By following the above procedure, we could calculate the rate of deactivation of ion pairs separated by a distance ρ which had a particular relative speed at $r_{12} = \infty$. The calculation was performed for both the positive and negative ion as ion 1. The following section shows how the recombination coefficient was calculated from these partial deactivation rates.

Calculation of the Recombination Coefficient

To set up this problem, we first imagine the ion-ion two body problem reduced to the equivalent one body problem in which one ion is stationary, and the other, assigned a mass $\mu_{12} = m_1 m_2/(m_1+m_2)$, sweeps out its trajectory. We can specify the state of this ion pair by saying that the square of its impact parameter is between b_i^2 and $b_i^2 + \Delta(b^2)$, where $\pi\Delta(b^2)$ is some increment in the target area. For a given b_i and a particular value of the initial relative kinetic energy $T_R(\infty)$, there will be a distance of closest approach R_i for the two ions, which is given implicitly by

$$b_i^2 = R_i^2\left(1 + \frac{e^2}{R_i T_R}\right)$$

It is important to realize that T_R and thus R_i are functions of $\gamma(\infty)$ for fixed magnitudes of $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_2$, and we have not yet

averaged over $\gamma(\infty)$. However, for a given value of T_R we can imagine the stationary particle to be surrounded by concentric spherical zones whose lesser radius is R_i, and whose greater radius is R_{i+1}, the distance of closest approach for those ions with an impact parameter defined by $b_i^2 + \Delta(b^2)$. Ions in the ith state will, in the absence of other collisions, pass through all zones $j > i$ two times: once each on the incoming and outgoing legs of the ion-ion collision. The problem is to calculate the rate at which deactivating collisions occur for ions in each of these zones, and to take account of the depletion of the ion concentration along the trajectory by collisions in zones encountered previously.

Let us consider the flux of ions in the ith state into the ith zone on the incoming leg of an ion-ion collision. This is given by

$$P_i = \pi(b_{i+1}^2 - b_i^2)g_{12}(1-F_i)[A^+][B^-]$$

where F_i is the fraction of the ion pairs originally in the ith state which has been deactivated in outer zones $j > i$. It is given by

$$F_i = \sum_{j=i+1}^{m-1} f(i,j)$$

where $f(i,j)$ is the fraction of ion pairs in the ith state deactivated in the jth zone, and m-1 is the index of the outermost zone in which deactivation occurs. The quantity $f(i,j)$ is the product of two factors: the probability that in the jth zone there will be a deactivation of an ion pair

in the ith state, and the probability that ions originally in the ith state have not been deactivated before reaching zone j. Thus

$$f(i,j) = \frac{k_3(j)[M]}{\left\langle \frac{1}{\tau_{ij}} \right\rangle + k_3(j)[M]} \left[1 - \sum_{k=i+1}^{m-1} f(i,k) \right]$$

where $k_3(j)$ is the sum of the rate constants for deactivation of the two ions characteristic of the jth zone. These were the $k_3(\rho)$, calculated as indicated in the earlier sections, with $\rho = R_j$. The quantity $\langle 1/\tau_{ij} \rangle$ is the average of the reciprocal time required for ions in the ith state to traverse the jth zone. The time required for ion to pass between any two radii was obtained from the standard mechanics[6] of the hyperbolic orbit, and averaged over the eccentricities appropriate for the ith state.

The fraction of ions in the ith state deactivated in the ith zone is

$$G_i = \frac{k_3(i)[M](1-F_i)}{\langle 1/\tau_{ii} \rangle + k_3(i)[M]}$$

where τ_{ii} is the time the ions spend in the ith zone.

The procedure applied to the outgoing leg of the collision is similar to the foregoing. Let $H(i,j)$ be the fraction of ion pairs initially in the ith state deactivated before they reach the jth zone on the outgoing leg. Then the fraction deactivated in the jth zone is

$$h(i,j) = \frac{k_3(j)[M][1-H(i,j)]}{\langle 1/\tau_{ij}\rangle + k_3(j)[M]}$$

and

$$H(i,j) = \sum_{\ell=i}^{j-1} h(i,\ell)$$

with

$$h(i,i) = F_i + G_i$$

Finally, the rate of deactivation of ion pairs in the ith state is D_i, where

$$D_i = H(i,m)\,\pi(b_{i+1}^2 - b_i^2)\,g_{12}[A^+][B^-]$$

Here $H(i,m)$ is the fraction of pairs deactivated before passing out of zone m-1, the outermost zone. Thus the total deactivation rate for ions with initial relative speed g_{12} is

$$\sum_{i=0}^{m-1} D_i.$$

The problem was completed by averaging over the relative speed. For fixed magnitudes of $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_2$ this is accomplished by averaging over $\gamma(\infty)$. The result is the total deactivation rate, which we set equal to $\alpha_t(A^+)(B^-)$.

Results and Discussion

In the evaluation of α_t the calculations were cut off at some maximum ion-ion impact parameter b_m. In an ideal situation, the values of $k_3(i)$ would rapidly diminish as i

increased so that ion-ion collisions with nearly the maximum impact parameter considered would not contribute significantly to the value of α_t. However, when the requirement for deactivation is simply

$$T_R'(\rho) \leq \frac{e^2}{\rho} \tag{10}$$

the value of α_t was still increasing when $b_m = 1500$ Å. Thus we found that it was not possible to calculate an absolute value of α_t when the deactivation requirement was Eq. (10) without making an arbitrary cut off of b_{12}. Nevertheless it was possible to calculate and draw some significance from relative values of α_t for the different inert gases for the various values of b_m.

We also calculated α_t by using a more severe requirement for deactivation:

$$T_R'(\rho) \leq \frac{e^2}{\rho} - E_D$$

where E_D is an extra amount of energy that must be lost in order to insure that the ions remain bound. This requirement is suggested by the observation that two ions whose total relative energy is zero or only slightly negative may undergo subsequent dissociating collisions. As the total relative energy of the ion pair diminishes, so does the chance of such dissociations. When E_D was set equal to kT, we found that no deactivation occurred for ion pairs with $b_{12} \geq 1500$ Å. Thus, for this deactivation criterion, α was independent of b_m if b_m was greater than 1500 Å.

Another general result of the calculation was the demonstration that the deactivation rate constant $k_3(\rho)$ depended on both the initial relative speed of the ions, and the distance ρ at which the deactivation occurred. This is shown in Fig. 3, where k_3 is plotted as a function of ρ for deactivation of an NO^+ NO_2^- pair by collision of NO^+ with an argon atom. For a given value of ρ and of the deactivation criterion, deactivation of ion pairs with small initial relative speeds proceeds fastest. This is not surprising, since it is clear from the mechanics that most collisions involve a small deflection and energy exchange. In this respect, it is interesting to note that our calculations of k_3 for other neutrals show that the relative values of k_3 for the different gases depend on $T_R(\infty)$. The ratio of k_3 for a heavy gas to that for a light gas diminishes as T_R diminishes. The principal reason for this is that kinematic factors limit the light neutrals to removing only a small fraction of the kinetic energy of a heavier ion, and prevent large ion deflections. As the energy that must be lost decreases these kinematic limitations become less important, and the differences in the relative efficiencies of the neutrals tend to diminish.

The contribution to α_t of ion-ion collisions with small relative speed tends to be reduced by the fact that the rate of such collisions decreases as g_{12} decreases. On the other hand, ions with smaller initial relative speed will tend to spend a longer time close to each other, and this increases the

total probability of deactivation. We find that this latter factor combined with the increase of k_3 for small values of g_{12} is large enough so that these smaller values of g_{12} make the largest contribution to α_t.

The increase of k_3 as ρ decreases is not difficult to rationalize. As the ions approach each other, their kinetic energies increase, and thus the fractional energy loss which must occur to give deactivation decreases. Elementary kinematics[6] shows that if the neutral is considered stationary, the cross section for a given fractional energy loss increases as the fractional loss decreases. We expect this effect to persist even in the deactivation problem where the neutral is moving. The contribution to α_t of these deactivations at small values of ρ is diminished because the ions remain close to each other for relatively short periods, and also because these close collisions generally involve smaller values of b_{12}, and are correspondingly less probable.

The third qualitative feature of Fig. 3 is that the deactivation rate decreases as E_D, the required binding energy, increases. This effect also has its explanation in the fact that the probability of a given energy transfer diminishes as the energy to be transferred increases.

The absolute values of α_t calculated for helium at a pressure of 10 mm are shown in Table II. Calculations were carried out for two values of the hard sphere radius s taken from Table I. The increase of α_t with b_m for $E_D < kT$ can be seen, as well as the decrease of α_t with increasing E_D and increasing ion mass.

Tables III, IV, and V give the calculated deactivation efficiencies of the various inert gases relative to helium for three choices of E_D and two different sets of ion masses. These relative efficiencies were found by taking the ratios of the values of α_t calculated for the gases at 10 mm pressure. It is clear that efficiencies depend on the value of b_m. For $E_D = 0$, the relative efficiencies of the heavier gases for the lighter ions are insensitive to b_m, but for the heavier ions the heavier neutrals tend to become less efficient as b_m increases. This latter trend is maintained when $E_D = 0.5$ kT, but reversed when $E_D = kT$. We can see also that as E_D increases, the efficiencies tend to become more sensitive to the identity of neutral, particularly for the heavier ion pair. This effect, like the dependence of k_3 on T_R, is probably due to the kinematic limitations imposed by the momentum conservation law on the ability of the lighter neutrals to remove sufficient energy for deactivation. In a system where the ion mass was well known, the experimental relative efficiencies of the inert gases might be used to determine a probable value of E_D.

The calculated values of the relative efficiencies are to be compared with the experimental values[1] found in Table VI. There is certainly general qualitative agreement between experiment and calculation. It is difficult to make a critical comparison because the importance of clustered ions in this system is not known at present. However, we can say that if the mass of the ions corresponds to $N_2O_3^+$, $N_2O_4^-$, or is greater, then the requirement that $E_D = kT$ makes the experimental and

calculated efficiencies disagree with each other. Even if the ions are not complexed, the choice of $E_D = kT$ is apparently least satisfactory, for it leads to an efficiency for hydrogen which is too low. The best agreement appears to result when it is assumed that $E_D = 0.5\ kT$, and that a mixture of ion masses is present.

It is important to notice that for all ion masses and deactivation requirements the calculated efficiencies of the neutrals increase as their masses increase. This is in contradiction to the predictions of the simplest approach to the energy loss problem, in which it is assumed that most efficient energy transfer occurs when the masses of the collision partners are the same. This is an idea valid when only the magnitude of the ion kinetic energy in a fixed coordinate system is important, and when the direction the ion takes after the collision is immaterial. This is not the case in the recombination problem, where a deflection without large energy transfer can lead to deactivation, as we have noted earlier.

We conclude from this comparison of experimental and calculated ion recombination rates that the collisional deactivation mechanism originally proposed by Thomson is essentially correct in its physical conception. The refinements we have introduced with the aid of machine calculation afford very encouraging predictions the relative values of α_t at the lower pressures. In addition, the examination of the detailed mechanics of ion recombination has revealed some qualitative explanations of the relative efficiencies of the various

deactivating gases, and has indicated the importance of the binding requirement. These ideas may find application in other recombination problems.

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Appendix

For the ion-induced dipole potential with a hard core Hassé[5] has shown how to express the deflection angle χ_{13} in terms of two parameters defined by

$$Y = \left(\frac{\mu_{13}}{\alpha' e^2}\right)^{1/2} b_{13}^2 g_{13}$$

$$Z = \left(\frac{\mu_{13}}{\alpha' e^2}\right)^{1/2} g_{13} s^2$$

where e is the electronic charge, α' is the polarizability of the neutral, and s is the core diameter. By using Hassé's equations, χ_{13} was calculated as a function of Y. Listed below in Table VII are the values of ΔY for various values of $\Delta|(\chi_{13}-m2\pi)|$. The rate constant k_χ for the formation of deflections in the region $\Delta|(\chi_{13}-m2\pi)|$ is given by

$$k_\chi = \pi\left(\frac{\alpha' e^2}{\mu_{13}}\right)^{1/2} \Delta Y$$

In this way the partial rate constants for deactivation can be calculated.

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Table I

Hard Sphere Core Parameter s

Gas	Ion Molecular Weight		
	30	46	76
He[a]	2.52 2.94	2.52 3.43	2.72 3.78
Ar	2.88 3.37	2.88 3.86	3.08 4.21
Kr	3.02 3.47	3.02 3.96	3.22 4.31
Xe	3.12 3.70	3.12 4.19	3.32 4.54
H_2	2.88 3.13	2.88 3.62	3.08 3.97
D_2	2.88 3.13	2.88 3.62	3.08 3.97
N_2	3.02 3.50	3.02 3.99	3.22 4.34

a. All distances in Å. First value is estimated from Goldschmidt's table, the second by using Lennard-Jones σ values.

Table II

Calculated values of α_t for NO-He Mixtures.[a]

b_m[b] (Å)	$E_D=0$		$E_D=0.5kT$		$E_D=kT$	
	G[c]	L-J[d]	G	L-J	G	L-J
			NO^+, NO_2^- Ion Pair			
400	0.40	0.48	0.20	0.24		
600	1.22	1.41	0.49	0.58	0.27	0.33
800	2.60	2.92	0.95	1.13	0.49	0.60
1000	4.81	5.34	1.60	1.93	0.69	0.84
1200	8.3	9.1	2.39	2.90	0.77	0.94
1500	16.5	18.0	3.62	4.43	0.79	0.97
			$NO(NO_2)^+$, $(NO_2)_2^-$ Ion Pair			
400	0.15	0.20	0.05	0.08		
600	0.52	0.62	0.19	0.27	0.10	0.16
800	1.27	1.50	0.44	0.65	0.16	0.26
1000	2.75	3.24	0.74	1.13	0.19	0.31
1200	5.18	6.22	0.99	1.54	0.19	0.31
1500			1.24	1.96	0.19	0.31

a. A total pressure of 10 mm is assumed, and α_t is given in cc/sec x 10^8.

b. Maximum value of impact parameter for deactivation.

c. Values of α_t when s was estimated from the Goldschmidt Table.

d. Values of α_t when s was estimated from Lennard-Jones σ values.

Table III

Relative third-body efficiencies for E_D=0.[a]

b_m	NO^+, NO_2^-		$N_2O_3^+$, $N_2O_4^-$		NO^+, NO_2^-		$N_2O_3^+$, $N_2O_4^-$	
(Å)	G	L-J	G	L-J	G	L-J	G	L-J
	Nitrogen				Argon			
400	4.0	3.3	6.0	4.8	3.9	3.2	6.2	4.9
600	4.3	3.7	5.9	5.1	4.0	3.4	6.0	5.1
800	4.4	3.9	5.3	4.6	4.1	3.6	5.4	4.7
1000	4.3	3.9	4.5	3.9	4.0	3.6	4.7	4.0
	Hydrogen				Krypton			
400	1.35	1.13	1.25	0.98	4.7	3.8	7.8	5.9
600	1.43	1.25	1.58	1.37	5.0	4.3	7.5	6.2
800	1.56	1.40	1.91	1.69	5.1	4.5	6.6	5.6
1000	1.73	1.57	1.94	1.71	5.0	4.4	5.5	4.6
	Deuterium				Xenon			
400	1.86	1.57	1.85	1.50	6.1	4.9	9.8	7.4
600	1.89	1.66	1.88	1.63	6.6	5.5	9.4	7.6
800	1.89	1.70	1.88	1.65	6.7	5.8	8.1	6.8
1000	1.89	1.72	1.87	1.64	6.5	5.7	6.8	5.6

a. Efficiency of He is taken as unity. Other notation as in Table II.

Table IV

Relative third-body efficiencies for $E_D=0.5k\ T$

b_m	NO^+, NO_2^-		$N_2O_3^+$, $N_2O_4^-$		NO^+, NO_2^-		$N_2O_3^+$, $N_2O_4^-$	
(Å)	G	L-J	G	L-J	G	L-J	G	L-J
	Nitrogen				Argon			
400	5.5	4.7			5.4	4.6		
600	5.9	5.0	7.6	5.6	5.8	4.9	8.7	6.3
800	5.4	4.5	5.7	4.0	5.2	4.3	6.6	4.6
1000	4.9	4.0	5.2	3.6	4.6	3.8	5.9	4.0
1200	4.4	3.6	5.5	3.7	4.1	3.3	6.0	4.0
1500			6.7	4.4			6.8	4.4
	Hydrogen				Krypton			
400	1.01	0.87			6.9	5.7		
600	1.26	1.10	1.59	1.19	7.6	6.3	11.7	8.1
800	1.45	1.24	1.34	0.98	7.0	5.7	9.0	6.0
1000	1.46	1.23	1.07	0.77	6.0	4.8	8.1	5.3
1200	1.36	1.13	0.91	0.64	5.1	4.1	8.1	5.2
1500			0.73	0.51			8.8	5.6
	Deuterium				Xenon			
400	1.70	1.47			9.0	7.3		
600	1.76	1.53	1.81	1.36	10.0	8.2	15.5	10.4
8800	1.81	1.55	1.81	1.33	9.0	7.3	11.5	7.5
1000	1.84	1.55	1.80	1.30	7.6	6.1	10.2	6.5
1200	1.84	1.55	1.80	1.27	6.3	5.1	10.2	6.3
1500			1.78	1.26			10.9	6.8

Table V

Relative third-body efficiencies for $E_D = k\ T$

b_m	NO^+,	NO_2^-	$N_2O_3^+$,	$N_2O_4^-$	NO^+,	NO_2^-	$N_2O_3^+$,	$N_2O_4^-$
(Å)	G	L-J	G	L-J	G	L-J	G	L-J
		Nitrogen				Argon		
600	6.3	5.2	7.4	5.0	6.1	5.0	9.0	6.1
800	5.3	4.4	7.4	4.9	5.1	4.2	8.4	5.6
1000	5.0	4.1	9.2	6.1	4.7	3.9	9.9	6.5
1200	5.2	4.3	11.8	8.0	5.0	4.0	12.4	8.2
1500	5.4	4.4	13.4	8.8	5.1	4.1	14.2	9.3
		Hydrogen				Krypton		
600	1.23	1.03	1.09	0.77	8.2	6.5	13.0	8.3
800	1.15	0.96	0.82	0.58	6.5	5.2	12.0	7.5
1000	0.96	0.80	0.70	0.49	5.8	4.7	13.6	8.5
1200	0.88	0.73	0.70	0.49	5.9	4.7	16.5	10.3
1500	0.86	0.71	0.70	0.49	6.0	4.8	18.5	11.5
		Deuterium				Xenon		
600	1.73	1.46	1.76	1.25	10.7	8.4	17.8	10.9
800	1.74	1.47	1.73	1.23	8.3	6.6	15.8	9.6
1000	1.73	1.46	1.72	1.22	7.3	5.8	17.6	10.6
1200	1.74	1.46	1.72	1.22	7.3	5.8	20.8	12.6
1500	1.76	1.47	1.72	1.22	7.3	5.8	22.9	13.8

Table VII

$\Delta|(\chi_{13}-m2\pi)|$ as a function of ΔY and Z

$\Delta|(\chi_{13}-m2\pi)|$ (degrees)	Z 0.30	0.90	1.55	2.0	3.0	4.0	6.0	8.0
2 to 10	4.51	4.51	4.51	4.49	4.49	4.18	2.25	0.302
10 to 20	1.104	1.135	1.099	1.087	0.741	0.118	0.137	0.202
20 to 30	0.532	0.563	0.523	0.527	0.145	0.174	0.233	0.257
30 to 40	.352	.372	.346	.272	.179	.222	.312	.404
40 to 50	.269	.278	.271	.159	.210	.266	.382	.502
50 to 60	.222	.225	.237	.169	.235	.302	.439	.577
60 to 80	.361	.363	.332	.371	.523	.678	.996	1.317
80 to 100	.290	.293	.310	.381	.544	.713	1.054	1.398
100 to 120	.238	.238	.282	.350	.506	.665	.988	1.312
120 to 140	.191	.181	.225	.281	.410	.540	.804	1.068
140 to 160	.142	.116	.144	.181	.266	.352	.524	.697
160 to 180	.119	.057	.052	.065	.093	.122	.182	.242

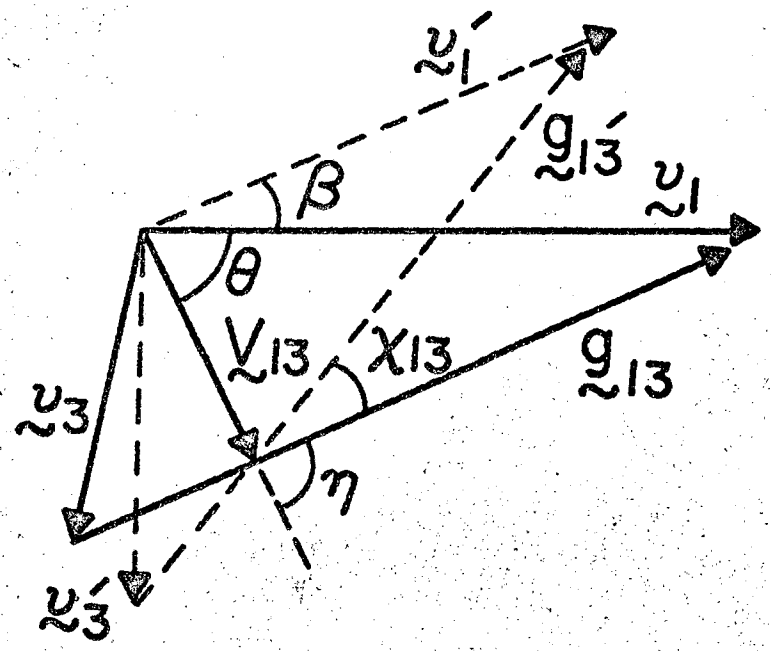

Fig. 1

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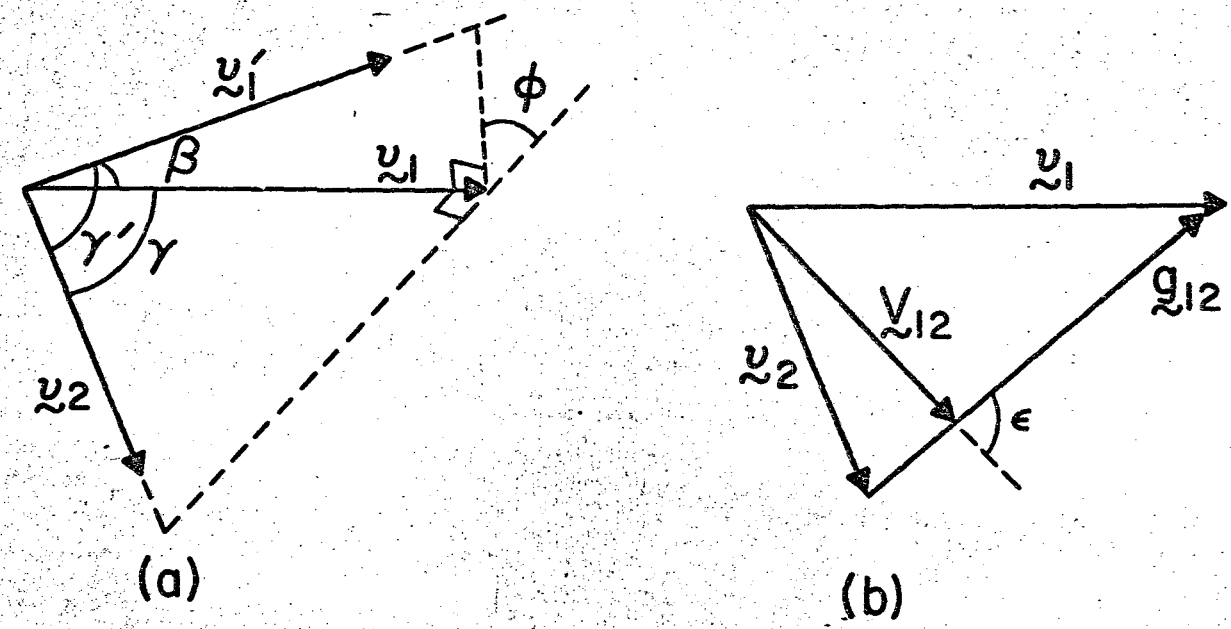

Fig. 2

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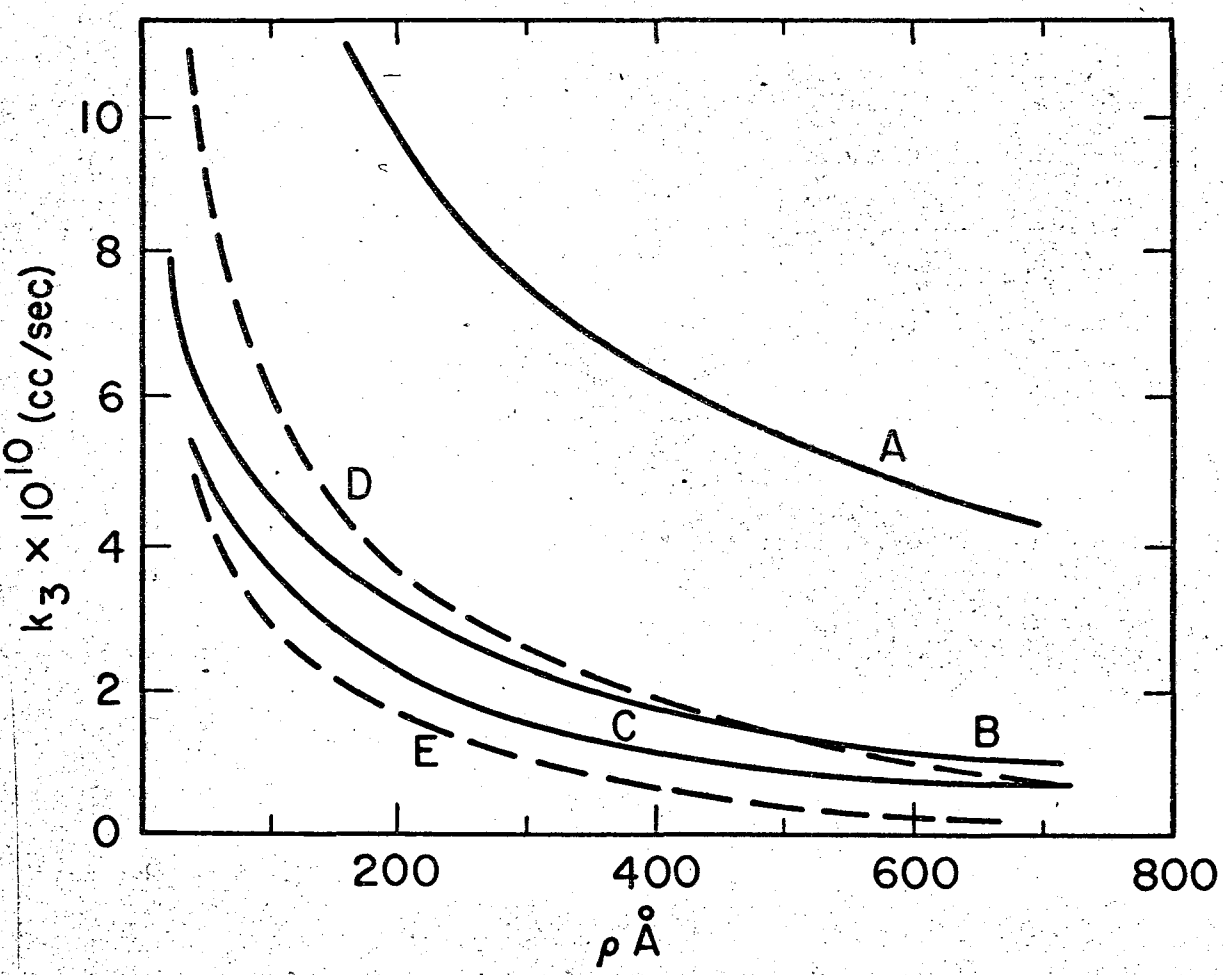

Fig. 3

MU-32614

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