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Calculation of Three-Body Ionic Recombination Rate

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The three-body ionic recombination rate at low densities is calculated for a slightly ionized gas by considering that the relaxation of the energy of molecules occurs by a "diffusion" process. The effective conductivity in the equivalent diffusion equation is the second moment of the energy transfer.

The moments are derived in closed form using classical mechanics and enable the recombination rate constant to be obtained. The agreement of the results with experimental data is good and suggests that the approach is useful even where relatively large energy transfers are involved.

I. INTRODUCTION

The three-body ionic recombination process $A^+ + B^- + C \rightarrow AB + C$ is of practical importance for phenomena occurring in the upper atmosphere, hypersonic flight, and gaseous discharges. The problem was first studied by Thomson[1] who suggested that recombination occurs if two oppositely charged ions pass close to one another and, while interacting, either ion collides with a neutral losing enough energy to it to bind the ion pair in an elliptic orbit. Eventually an electron is transferred from the negative ion to the positive ion, and recombination is complete. Thomson calculated a recombination rate taking simple averages over the collisions. His analysis has been further refined by Natanson,[2] Brueckner,[3] and Feibelman[4] who followed the collisions with a Monte Carlo calculation and considered the requirement of stability of the recombined ion pair against further collisions with the neutral gas.

The relaxation of the molecules in the case of small energy transfers shows the behavior of a random walk up and down the energy ladder and suggests that the process can be described by an equivalent diffusion equation. This idea gives the process a simple physical meaning as we can think of the ion pairs as diffusing through an imaginary permeable membrane at the dissociation limit. The dissociated pairs lose energy to the neutral particles and eventually go through the membrane and down the energy ladder. Keck and Carrier[5] derived an equivalent diffusion equation for this process from the master equation and showed that the effective conductivity is the second moment of the energy transfer. They also showed that the first moment should be one-half of the derivative of the second moment for the theory to be valid.

In this investigation we calculate the moments in closed form using classical mechanics for a three-body system of arbitrary masses. In special cases we demonstrate the validity of the diffusion theory and use its results to calculate the recombination rate constant.

Recombination has been also treated as a diffusion process by Pitaevskii[6] and Gurevich,[7] and there is agreement with our results in the case of electron–ion recombination in a neutral background gas.

II. DIFFUSION THEORY

Keck and Carrier have shown that the relaxation of molecules in a background of inert atoms can be described by the equivalent diffusion equation

$$N_e \frac{\partial X}{\partial t} = \frac{1}{2} \frac{\partial}{\partial E} \left(\Delta_2 \frac{\partial X}{\partial E} \right), \tag{1}$$

where E is the energy of a molecule with the dissociation limit as origin, $N_e(E)dE$ is the equilibrium concentration of molecules in an energy band dE at E, $X(E, t) = N(E, t)/N_e(E)$ is the ratio of the actual concentration of molecules at a given level to the equilibrium concentration, and

$$\Delta_n(E) = \int_{-\infty}^{\infty} R(E, E')(\Delta E)^n dE' \tag{2}$$

is the nth moment of the energy transfer $\Delta E = (E' - E)$ with respect to the equilibrium transition rate $R(E, E')$.

The steady-state solution is obtained by setting (1) equal to zero and integrating. The distribution function is then

$$X(E) = X(-D, t)\chi_D(E) + X(0, t)\chi_R(E), \tag{3}$$

where

$$\chi_D(E) = 1 - \chi_R(E) = \int_E^0 \frac{dE'}{\Delta_2(E')} \bigg/ \int_{-D}^0 \frac{dE'}{\Delta_2(E')}$$

and D is the dissociation energy of the recombined ion pair.

In general $\Delta_2(E)$ has a relatively strong minimum at an energy $E^* < 0$. It follows that for $E < E^*$, $\chi_D(E) \approx 1$ while for $E > E^*$, $\chi_D(E) \approx 0$. Thus E^* may be interpreted as the location of a "bottleneck" on the energy

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[2] G. L. Natanson, Zh. Tekhn. Fiz. **29**, 1486 (1959) [Soviet Phys.—Tech. Phys. **4**, 1373 (1960)].

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[7] A. V. Gurevich and L. P. Pitaevskii, Soviet Phys.—JETP **19**, 4 (1964).

ladder which effectively divides bound and free ion pairs.

Substituting (3) into (1) and integrating from $-D$ to E^*, we obtain the rate equation

$$d[\mathrm{AB}]/dt=\alpha[\mathrm{A}][\mathrm{B}]-\alpha K_e[\mathrm{AB}],$$

where

$$[\mathrm{AB}]\equiv\int_{-D}^{E^*} N_eXdE\approx X(-D,t)[\mathrm{AB}]_e$$

is the concentration of bound ion pairs,

$$\alpha=\left(2[\mathrm{A}]_e[\mathrm{B}]_e\int_{-D}^{0}\frac{dE}{\Delta_2(E)}\right)^{-1} \qquad (4)$$

is the steady-state recombination rate constant for the reaction, $K_e=[\mathrm{A}]_e[\mathrm{B}]_e/[\mathrm{AB}]_e$ is the equilibrium constant, and we have used the boundary condition $X(0,\,t)=[\mathrm{A}][\mathrm{B}]/[\mathrm{A}]_e[\mathrm{B}]_e$ which is appropriate in this case due to the effectively infinite transition rate at the dissociation limit of a Coulomb oscillator.

We have seen the significance of Δ_n for $n=2$, but the cases $n=0$ and 1 also have importance. Δ_0 is the collision rate per unit energy per unit volume, so that

$$\Delta_2/\Delta_0=\langle(\Delta E)^2\rangle \qquad (5)$$

is the mean-square value of the energy transfer per collision. In addition a condition for the validity of (1) is

$$\Delta_1\approx\tfrac{1}{2}\partial\Delta_2/\partial E. \qquad (6)$$

III. THE CALCULATION OF THE MOMENTS

A. The Model

The collision geometry is shown in Fig. 1. 1 and 2 are singly charged particles whose interaction potential obeys a simple Coulomb law. 3 is a neutral particle, and we assume that it hits one end of the "dumbbell" impulsively while leaving the other end unaffected.

Consider 3 hitting 1, and let unprimed and primed quantities represent conditions before and after the collision. The change of the relative kinetic energy of 1 and 2 due to the collision is given by

$$\Delta E_{12}=\tfrac{1}{2}\mu_{12}(v_{12}'^2-v_{12}^2),$$

which in terms of the initial center-of-mass momenta becomes

$$\Delta E_{12}=\frac{2\mu_{12}}{\mu_3^2}\left(\frac{m_3}{m_1+m_3}\right)^2\left(p_{3x}-\frac{\mu_3}{m_1}\,p_{12x}\right)\left(p_{3x}+\frac{m_1}{\mu_{12}}\,p_{12x}\right). \qquad (7)$$

The reduced masses are defined as $\mu_{12}=m_1m_2(m_1+m_2)^{-1}$ and $\mu_3=m_3(m_1+m_2)/M$, where $M=m_1+m_2+m_3$. A similar expression can be obtained for the situation in which 3 hits 2 by interchanging the subscripts 1 and 2.

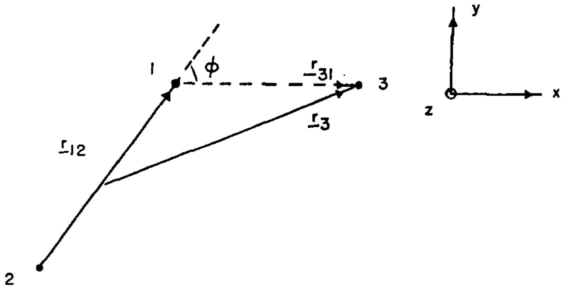

FIG. 1. Coordinate system used to describe collisions.

B. The Moments of the Energy Transfer

The moments for the 1–3 collisions are defined as

$$\Delta_n^{(1)}=-\rho_0\int_{v_{31x}\le 0}(\Delta E_{12})^n\exp\left(\frac{-H}{kT}\right)4\pi a_{13}^2v_{31x}d\mathbf{p}_3 2\pi r_{12}^2 \times\frac{\partial r_{12}}{\partial E_{12}}\,d\cos\phi d\mathbf{p}_{12}, \qquad (8)$$

where $H=E_{12}+\mathbf{p}_3^2/(2\mu_3)$ is the Hamiltonian for the center-of-mass system, $E_{12}=\mathbf{p}_{12}^2/(2\mu_{12})-\bar{e}^2/r_{12}$ is the relative energy of 1 and 2, $v_{31x}=p_{3x}/\mu_3-p_{12x}/m_1$ is the relative velocity of 3 and 1,

$$\rho_0=[\mathrm{A}]_e[\mathrm{B}]_e[\mathrm{C}](2\pi\mu_3kT)^{-3/2}(2\pi\mu_{12}kT)^{-3/2}$$

is the density of points in phase space, a_{13} is an assumed collision diameter for ion and neutral, and $\bar{e}$ is the electronic charge.

The problem becomes more manageable if we introduce the following dimensionless parameters:

$$\mathbf{f}=\mathbf{p}_3/(2\mu_3kT)^{1/2},\qquad \mathbf{g}=\mathbf{p}_{12}/(-2\mu_{12}E_{12})^{1/2},$$

$$\epsilon=-E_{12}/kT,\qquad \delta=D/kT,$$

and

$$\gamma_1=\mu_3\mu_{12}/m_1^2=m_2m_3/m_1M.$$

This substitution leads to

$$\Delta E_{12}=kT\beta_1[f_x-(\epsilon\gamma_1)^{1/2}g_x][f_x+(\epsilon/\gamma)^{1/2}g_x]$$

and

$$v_{31x}=\tfrac{1}{2}\pi^{1/2}\bar{c}_3[f_x-(\epsilon\gamma_1)^{1/2}g_x],$$

where

$$\beta_1=4m_1m_2m_3M/(m_1+m_2)^2(m_1+m_3)^2$$

and

$$\bar{c}_3=(8kT/\pi\mu_3)^{1/2}$$

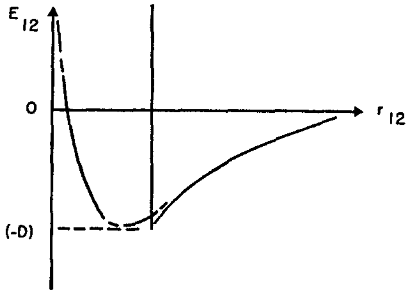

FIG. 2. Potential-energy diagram showing cutoff and comparison with realistic (dashed) curve.

is the mean speed for the collision. Thus (8) becomes

$$\Delta_n^{(1)} = -4(kT)^{n-1}\beta_1{}^n R_1(\pi\epsilon)^{-5/2}e^{\epsilon}$$
$$\times\int_{v_{31x}\leq 0}\frac{[f_x+(\epsilon/\gamma_1)^{1/2}g_x]^n[f_x-(\epsilon\gamma_1)^{1/2}g_x]^{n+1}}{(1+g^2)^4}$$
$$\times e^{-f^2}d\mathbf{f}d\mathbf{g}d\cos\phi, \quad (9)$$

where $R_1=(\pi a_{13}{}^2)(\pi r_T{}^3)\bar{c}_3[\mathrm{A}]_e[\mathrm{B}]_e[\mathrm{C}]$ is the three-body collision rate per unit volume and $r_T=\bar{e}^2/kT$ is the Thomson radius.

It is now clear, from (9), that we are going to encounter a logarithmic divergence for the case $n=2$. To handle this problem, we cut the integration off at $\bar{e}^2/r_{12}=D$. The potential-energy curve now appears as in Fig. 2, compared with a realistic curve. Thus the requirements $-\bar{e}^2/r_{12}=E_{12}-p_{12}{}^2/2\mu_{12}\geq -D$, and $v_{31x}\leq 0$ produce the conditions $-(\delta/\epsilon-1)^{1/2}\leq g_x\leq(\delta/\epsilon-1)^{1/2}$ and $f_x\leq(\epsilon\gamma_1)^{1/2}g_x$, which are shown on the phase plane in Fig. 3. There are no restraints on p_{3x}, p_{3y}, p_{3z}, and their range is $-\infty$ to $+\infty$, while $0\leq\phi\leq\pi$.

Integrating (9) for all quantities except x-momenta terms and adding the contributions from the two ends of the dumbbell, we have

$$\Delta_n=(kT)^{n-1}\epsilon^{-5/2}e^{\epsilon}\sum_{j=1,2}[R_j\beta_j{}^n I_n(\epsilon,\gamma_j)], \quad (10)$$

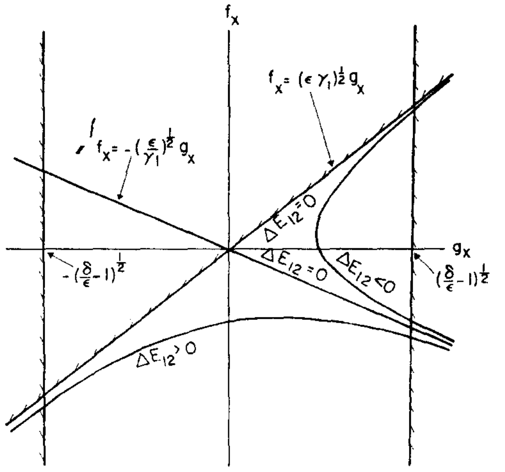

FIG. 3. X-momentum plane showing limits of integration. Domain of integration is inside hatched lines.

where

$$I_n(\epsilon,\gamma)=-\frac{8}{3\pi^{1/2}}\int_{-(\delta/\epsilon-1)^{1/2}}^{(\delta/\epsilon-1)^{1/2}}\int_{-\infty}^{(\epsilon\gamma)^{1/2}g_x}\left[f_x+\left(\frac{\epsilon}{\gamma}\right)^{1/2}g_x\right]^n$$
$$\times[f_x-(\epsilon\gamma)^{1/2}g_x]^{n+1}\left[(1+g_x{}^2)^{-3}-\left(\frac{\epsilon}{\delta}\right)^3\right]$$
$$\times\exp(-f_x{}^2)df_x dg_x. \quad (11)$$

We note that the logarithmic terms only enter in Δ_2, so we can neglect the terms involving δ for the calculation of Δ_0 and Δ_1. After lengthy, but straightforward manipulation of (11), the following results are obtained:

$$I_0(\epsilon,\gamma)=(\gamma\epsilon)^{1/2}+(\tfrac{1}{2}-\tfrac{1}{3}\gamma\epsilon)J(\gamma\epsilon), \quad (12)$$

$$I_1(\epsilon,\gamma)=(\gamma\epsilon)^{1/2}(-1+\tfrac{2}{3}\epsilon)+[-\tfrac{1}{2}+\tfrac{1}{3}(\gamma+1)\epsilon]J(\gamma\epsilon), \quad (13)$$

$$I_2(\epsilon,\gamma)=2(\gamma\epsilon)^{1/2}\{1+[(1/6\gamma)-\tfrac{1}{6}\gamma-1]\epsilon-\epsilon^2\}$$
$$+\{1+[(1/6\gamma)-\tfrac{1}{2}\gamma-1]\epsilon+\tfrac{4}{3}\epsilon^2\}J(\gamma\epsilon)$$
$$+\tfrac{4}{3}\epsilon^2(\gamma\epsilon)^{1/2}[\ln\gamma\delta-G(\gamma\epsilon)], \quad (14)$$

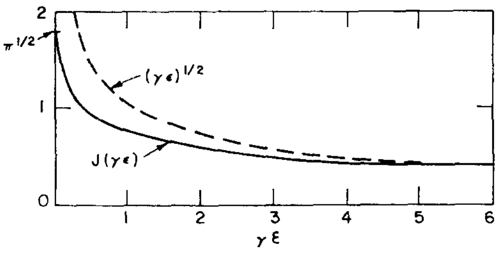

FIG. 4. Function $J(\gamma\epsilon)$ appearing in Eq. (14).

where

$$J(\gamma\epsilon)=e^{\gamma\epsilon}\int_{\gamma\epsilon}^{\infty}s^{-1/2}e^{-s}ds$$
$$=\pi^{1/2}: \qquad \gamma\epsilon\ll 1$$
$$=(\gamma\epsilon)^{-1/2}: \qquad \gamma\epsilon\gg 1$$

as shown in Fig. 4, and

$$G(\gamma\epsilon)=\tfrac{1}{3}+\ln(\gamma\epsilon)+\pi^{-1/2}\int_0^{\infty}\ln\left[1+\frac{s}{(\gamma\epsilon)}\right]s^{-1/2}e^{-s}ds$$
$$=-1.63: \qquad \gamma\epsilon\ll 1$$
$$=\tfrac{1}{3}+\ln\gamma\epsilon+\tfrac{1}{2}(\gamma\epsilon)^{-1}: \qquad \gamma\epsilon\gg 1$$

as shown in Fig. 5. As (ϵ/δ) is expected to be small, terms of order (ϵ/δ) and above are neglected.

IV. SPECIAL CASES

A. $m_3\ll m_1\sim m_2$; $\gamma_1\sim\gamma_2\to 0$

This is the case of heavy ions in the presence of a light catalyst. Adding contributions from both ends of the dumbbell

$$\Delta_0=\tfrac{1}{2}\pi^{1/2}(kT)^{-1}e^{\epsilon}\epsilon^{-5/2}\sum_{j=1,2} R_j, \qquad (15)$$

$$\Delta_1=4\pi^{1/2}e^{\epsilon}(\tfrac{1}{3}\epsilon^{-3/2}-\tfrac{1}{2}\epsilon^{-5/2})\sum_{j=1,2}\gamma_j R_j, \qquad (16)$$

$$\Delta_2=(8/3)\pi^{1/2}(kT)e^{\epsilon}\epsilon^{-3/2}\sum_{j=1,2}\gamma_j R_j. \qquad (17)$$

From (16) and (17) we see that

$$\Delta_1=\frac{(\partial\Delta_2/\partial\epsilon)}{(2kT)},$$

and (6) is satisfied, so in this case we can use the results of the diffusion theory. Equations (15) and (17) indicate that

$$\begin{aligned}\Delta_2/\Delta_0&=\langle(\Delta E_{12})^2\rangle\\&=16\epsilon(kT)^2\sum_{j=1,2}(\gamma_j R_j)/3\sum_{j=1,2}R_j,\end{aligned}$$

and the mean-square value of the energy transfer per collision is small. The behavior of Δ_0, Δ_1, and Δ_2 are shown in Fig. 6. The distribution function for recombination found from (3) is

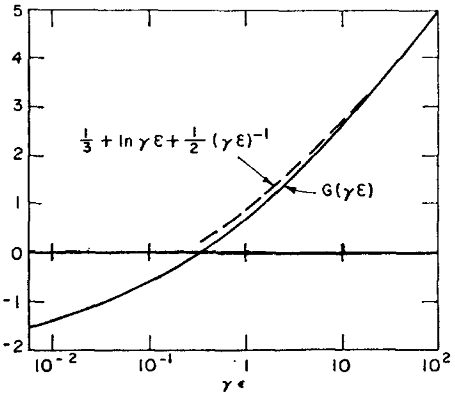

FIG. 5. Function $G(\gamma\epsilon)$ appearing in Eq. (14).

$$\begin{aligned}\chi_R(\epsilon)&=\int_{\epsilon}^{\delta}\eta^{3/2}e^{-\eta}d\eta\bigg/\int_0^{\delta}\eta^{3/2}e^{-\eta}d\eta\\&=1-\Gamma(\tfrac{5}{2},\epsilon)/\Gamma(\tfrac{5}{2})\end{aligned}$$

as δ is effectively infinite. $\chi_R(\epsilon)$ is plotted in Fig. 7.

From (4) we obtain the recombination rate constant

$$\begin{aligned}\alpha&=\tfrac{4}{3}\pi^{1/2}\sum_{j=1,2}\gamma_j R_j\bigg/\left([\mathrm{A}]_e[\mathrm{B}]_e\int_0^{\delta}\epsilon^{3/2}e^{-\epsilon}d\epsilon\right)\\&=\tfrac{16}{9}\pi\left(a_{13}{}^2\frac{m_2}{m_1}+a_{23}{}^2\frac{m_1}{m_2}\right)(\pi r_T{}^3)\left(\frac{8kT}{\pi(m_1+m_2)}\right)^{1/2}\\&\qquad\times\left(\frac{m_3}{M}\right)^{1/2}[\mathrm{C}]. \qquad (18)\end{aligned}$$

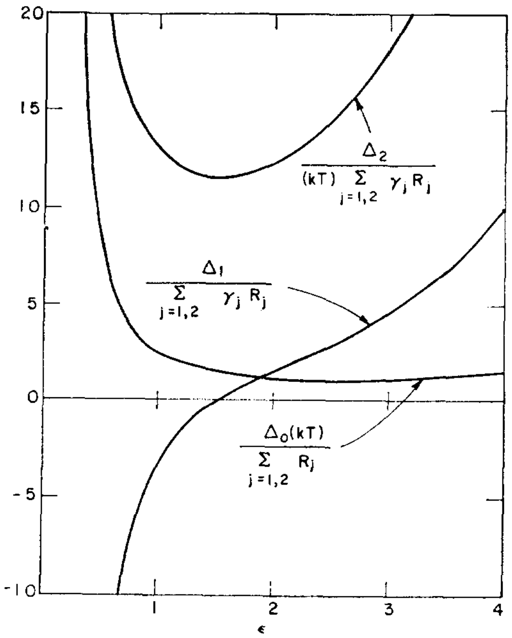

FIG. 6. Moments of energy transfer for case 1, $m_3 \ll m_1 \sim m_2$, i.e., light catalyst.

B. $m_2 \ll m_1 \sim m_3$; $\gamma_1 \rightarrow 0$, $\gamma_2 \rightarrow \infty$

This is the problem of electron–ion recombination in the presence of a neutral gas which Pitaevskii[6] investigated in his paper, and his result agrees exactly with the one below.

It is found that collisions of 3 with 2 give the dominant contributions to the moments

$$\Delta_0=\tfrac{2}{3}\gamma_2{}^{1/2}R_2(kT)^{-1}e^{\epsilon}\epsilon^{-2}, \qquad (19)$$

$$\Delta_1=(8/3)\gamma_2{}^{-1/2}R_2e^{\epsilon}(\epsilon^{-1}-\epsilon^{-2}), \qquad (20)$$

$$\Delta_2=(16/3)\gamma_2{}^{-1/2}R_2(kT)e^{\epsilon}\epsilon^{-1}. \qquad (21)$$

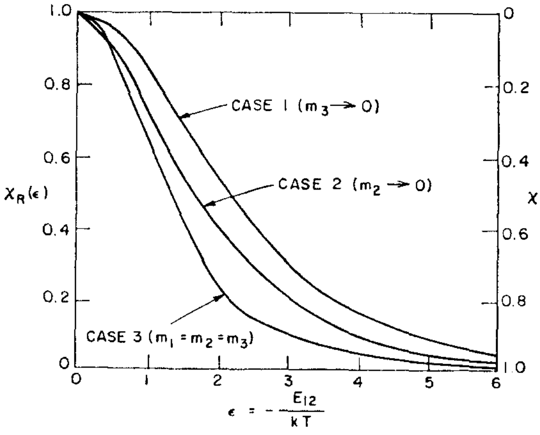

FIG. 7. Steady-state distribution functions during reaction. Left scale refers to recombination with no dissociation; right scale to dissociation with no recombination.

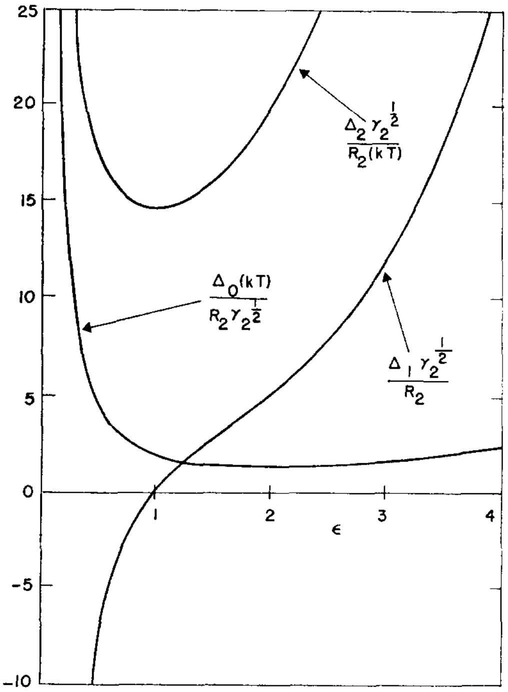

FIG. 8. Moments of energy transfer for Case 2, $m_2 \ll m_1 \sim m_3$, i.e., one light ion.

In this case also we see that

$$\Delta_1 = \frac{(\partial \Delta_2 / \partial \epsilon)}{(2kT)},$$

and we are able to use the results of the diffusion theory again. Also $\Delta_2/\Delta_0 = 8\gamma_2^{-1}\epsilon(kT)^2$, so the mean-square value of the energy transfer per collision is small. Figure 8 shows the character of Δ_0, Δ_1, and Δ_2.

The distribution function for recombination is found from (3),

$$\chi_R(\epsilon) = \int_\epsilon^\delta \eta e^{-\eta} d\eta \Big/ \int_0^\delta \eta e^{-\eta} d\eta$$
$$= (1+\epsilon) e^{-\epsilon},$$

since δ is again effectively infinite. $\chi_R(\epsilon)$ is plotted in Fig. 7.

Use of (4) gives the recombination rate constant

$$\alpha = \tfrac{8}{3}\gamma_2^{-1/2} R_2 \Big/ \left([\mathrm{A}]_e [\mathrm{B}]_e \int_0^\delta \epsilon e^{-\epsilon} d\epsilon \right)$$
$$= \tfrac{8}{3}(\pi a_{23}^2)(\pi r_T^3) \left(\frac{m_2}{m_1}\right)^{1/2} \left(\frac{m_1+m_3}{m_3}\right) \left(\frac{8kT}{\pi m_1}\right)^{1/2} [\mathrm{C}], \quad (22)$$

which is identical to Pitaevskii's result for the case $m_1 = m_3$.

C. $m_1 = m_2 = m_3$; $\gamma_1 = \gamma_2 = \frac{1}{3}$

This is the case of three-body recombination with the

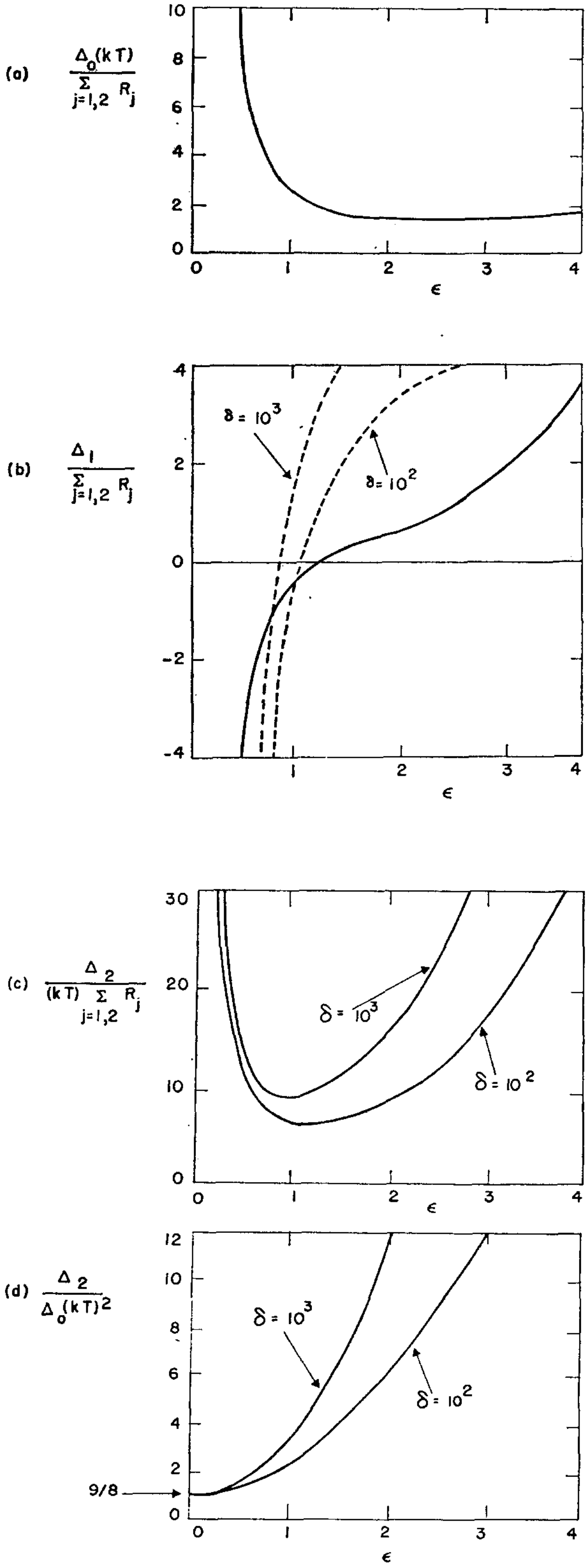

FIG. 9. Moments of energy transfer for Case 3, $m_1 = m_2 = m_3$, i.e., matched particles. The dashed curves in (b) are one-half the derivatives of the curves in (c) and show that condition (6) is not fulfilled.

three particles all of equal mass. We get the following results:

$$\Delta_0 = \sum_{j=1,2} R_j (kT)^{-1} e^{\epsilon} [3^{-1/2}\epsilon^{-2} + (\tfrac{1}{2}\epsilon^{-5/2} - \tfrac{1}{9}\epsilon^{-3/2}) J(\tfrac{1}{3}\epsilon)], \tag{23}$$

$$\Delta_1 = (\tfrac{3}{4})^{1/2} \sum_{j=1,2} R_j e^{\epsilon} \{ -\epsilon^{-2} + \tfrac{2}{3}\epsilon^{-1} + 3^{1/2}[-\tfrac{1}{2}\epsilon^{-5/2} + (4/9)\epsilon^{-3/2}] J(\tfrac{1}{3}\epsilon) \}, \tag{24}$$

$$\Delta_2 = (\tfrac{3}{16})^{3/2} (kT) e^{\epsilon} \sum_{j=1,2} R_j [2\epsilon^{-2} - \tfrac{8}{9}\epsilon^{-1} - 2 + 3^{1/2}(\epsilon^{-5/2} - \tfrac{2}{3}\epsilon^{-3/2} + \tfrac{4}{3}\epsilon^{-1/2}) J(\tfrac{1}{3}\epsilon) + \tfrac{4}{3}(\ln\tfrac{1}{3}\delta - G(\tfrac{1}{3}\epsilon) \}. \tag{25}$$

The variation of the amounts with energy and with the value of the cutoff is shown in Fig. 9. Δ_1 is compared with

$$\frac{(\partial \Delta_2/\partial \epsilon)}{(2kT)},$$

and we see how Δ_2/Δ_0 varies with energy and cutoff and that it is no longer small.

For the general case of $m_1 \sim m_2 \sim m_3$, we see from (14) and (25) that for $\epsilon \to 0$, the leading term of Δ_2 is

$$\Delta_{20}(\epsilon) = \pi^{1/2}(kT) e^{-5/2} e^{\epsilon} \sum_{j=1,2} (R_j \beta_j^2),$$

while for $\epsilon \to \infty$, the leading term is

$$\Delta_{2\infty}(\epsilon) = \tfrac{4}{3}(kT) e^{\epsilon} \sum_{j=1,2} [R_j \beta_j^2 \gamma_j^{1/2} \ln(\gamma_j \delta)].$$

Thus, to a reasonable approximation, we can write

$$\begin{aligned} \tilde{\Delta}_2(\epsilon) &= \Delta_{20}(\epsilon): \quad \epsilon < \epsilon^* \\ &= \Delta_{2\infty}(\epsilon): \quad \epsilon \geq \epsilon^*, \end{aligned} \tag{26}$$

where $\Delta_{20}(\epsilon^*) = \Delta_{2\infty}(\epsilon^*)$. In practice ϵ^* is found to be of order unity.

TABLE I. Recombination by: $NO^+ + NO_2^- + C$ (the molecular weights of NO^+ and NO_2^- are 30 and 46).

		$(\rho_0/\rho)\alpha \times 10^6$ cm^3/sec		
C	Molecular weight of C	a	b	c
H_2	2	0.76	0.67	
D_2	4	0.91	0.94	
He	4	0.76	0.72	
Ne	20	2.2	1.7	3.6
N_2	28	2.7	2.4	5.6
Ar	40	3.0	2.5	6.3
Kr	84	3.2	3.4	8.8
Xe	131	4.6	3.9	9.9

[a] Experimental data of Mahan and Person at 300°K.

[b] Calculated three-body recombination rate constant using (18) and Goldschmidt values[8] of a_{13} and a_{23}.

[c] Calculated three-body recombination rate constant using (27), $\delta = 100$, and Goldschmidt values of a_{13} and a_{23}.

TABLE II. Comparison of the values of the three-body recombination rate constant obtained by the diffusion theory for the reaction $(O_2^+ + O_2^- + O_2 \rightarrow O_4^* + O_2)$ at 18°C with the results of other work.

	$(\rho_0/\rho)\alpha \times 10^6$ cm^3/sec
Sayers[a] (exptl.)	7.3
Thomson[b]	12.2
Natanson[c]	7.7
Brueckner[d]	0.39
Feibelman[e]	5.3
Diffusion theory[f]	9.9

[a] See Ref. 9.

[b] See Ref. 1.

[c] See Ref. 2.

[d] See Ref. 3.

[e] See Ref. 4.

[f] The diffusion theory results are calculated using Goldschmidt collision diameters, and $\delta = 400$.

The distribution function for recombination is found from (3) and (26),

$$\chi_R(\epsilon) \approx 1 - \int_0^{\epsilon} \frac{d\eta}{\tilde{\Delta}_2(\eta)} \Big/ \int_0^{\delta} \frac{d\eta}{\tilde{\Delta}_2(\eta)}.$$

$\chi_R(\epsilon)$ is compared with the other recombination distribution functions in Fig. 7.

From (4) and (26), we obtain the recombination rate constant

$$\alpha \approx \left[2[\mathrm{A}]_e[\mathrm{B}]_e(kT) \left(\int_0^{\epsilon^*} \frac{d\eta}{\Delta_{20}(\eta)} + \int_{\epsilon^*}^{\delta} \frac{d\eta}{\Delta_{2\infty}(\eta)} \right) \right]^{-1}. \tag{27}$$

V. RESULTS AND DISCUSSION

We have compared the experimental measurements of the three-body recombination rate constant of photoionized nitric oxide obtained by Mahan and Person,[8] with values calculated using the results of the diffusion theory. The positive ion in the process was NO^+, while the negative was NO_2^-, and the recombination was observed with the dilute ionized gas in a variety of background gases with a range of molecular weights (Table I). We see that (18), which was derived strictly for the situation in which the third particle was much lighter than the other two, gives good agreement, not only in the intended range, but for all of the neutral gases. Equation (27) is applicable for situations when the three masses are approximately matched and shows some agreement with the experimental data. We can conclude that (18) is a good working formula over a wide range of catalysts, while (27) is useful with an appropriate choice of δ.

The results of the diffusion theory were also used to calculate the three-body recombination rate constant for the important case of oxygen ions in a background of either oxygen molecules or atoms. This was the

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[8] B. H. Mahan and J. C. Person, J. Chem. Phys. **40**, 10 (1964)

specific problem investigated by Brueckner[3] and Feibelman,[4] and our result is compared with the previous work in Table II. In applying (27) to this situation, we use a binding energy of about 10 eV which corresponds to $\delta = 400$ at room temperature. We see that the value of the recombination rate constant given by (27) compares favorably with Sayers'[9] experimental result and Feibelman's numerical calculation.

VI. CONCLUSIONS

The advantage of this method of calculation has been to produce general analytical forms for the three-body ionic recombination rate constant, which display its functional dependence on the masses of the three particles involved in the process. Confidence in this relationship has been strengthened by the good agreement of our results with the experimental data of Mahan and Person.[8] The calculated distribution function for recombination showed the energy levels empty up to the "bottleneck" and fully populated above; while the distribution function for dissociation had the energy levels fully populated up to the "bottleneck" and empty above. The "bottleneck" in every case was one or two units of (kT) below the dissociation limit. We have also seen that although small energy transfers per collision are the condition for applying the diffusion theory to this problem, useful results can be obtained by applying the approach to situations not strictly within these limitations.

The case of matched particles, where the energy transfers per collision were not small, was not suitable for the diffusion theory approach. This problem could be more suitably treated by calculating directly the transition rates $R(\epsilon', \epsilon)$ and solving the integral equation.

Further refinements to our calculations might include molecules with internal degrees of freedoms, for example, rotation in the case of diatomic molecules, and the possibility of collisions between ions.

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[9] J. Sayers, in *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), p. 275.

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Mercury-Photosensitized Decomposition of Ketene as a Source of Triplet Methylene*

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Mercury [Hg $6(^3P_1)$]-photosensitized decomposition of ketene has been investigated at room temperature and at various pressures of ketene from the point of view of its utilization as a convenient source of triplet methylene. The relative quenching cross section of ketene has been determined and an analysis of the likely extent of direct absorption of light by ketene at 2537 Å in competition with the absorption by mercury atoms has been made. Some aspects of the reaction mechanism are discussed.

In an earlier publication from our laboratory[1] it was shown that methylene in its ground electronic state, the triplet $CH_2(^3\Sigma_g)$, is a product of the mercury [Hg $6(^3P_1)$]-photosensitized decomposition of ketene. The photosensitized reaction therefore provides a useful source of triplet methylene. However, the reaction itself has never been examined in detail and a number of important questions remained unanswered. For example, it was not known how efficiently ketene could compete with other components of a reaction mixture for the excited mercury atoms since its quenching cross section was not determined. Similarly, since both mercury and ketene can absorb the resonance line of mercury at 2537 Å, it is important to assess what fraction of the incident radiation is likely to be absorbed directly by ketene as opposed to the mercury-photosensitized transfer of the energy of radiation. Any direct absorption by ketene at this wavelength will result in contamination by the singlet methylene $CH_2(^1A_1)$ and it is therefore necessary to know how serious such an interference is likely to be. Obviously, it is also desirable to obtain as much information as possible regarding the primary and secondary chemical reactions in this process. In the present paper we report the results of our further study of the mercury-photosensitized decomposition of ketene in an attempt to provide answers to some of the outstanding questions.

EXPERIMENTAL

The mercury [Hg $6(^3P_1)$]-photosensitized decomposition of ketene was studied at room temperature (25°±2°C) in a conventional high-vacuum apparatus. Three reaction vessels were used alternatively: (I) a circulating reactor of total volume of 403 ml, consisting of a cylindrical quartz cell 5 cm i.d., and 10 cm long connected to an all-glass circulating pump supported on Teflon bearings; (II) a small static reactor of

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[1] F. J. Duncan and R. J. Cvetanović, J. Am. Chem. Soc. 84, 3593 (1962).