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GASEOUS ION RECOMBINATION. V

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September 1967

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Gaseous Ion Recombination. V

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Pitaevski's formulation of the three-body ion-electron recombination rate constant based on the Fokker-Planck equation is modified so as to apply to the termolecular association of gaseous ions. The theory is expected to be valid when the collisional energy changes are small compared to the kinetic energy of the recombining ions, which occurs when the mass of the neutral is much less than the masses of the ions. The calculated and measured rate constants for such systems are in substantial agreement.

The termolecular recombination of gaseous ions is an instructive example of the three body association process. In contrast to the recombination of neutral atoms, ion recombination is dominated by the energy transfer mechanism,[1] only one well known potential energy surface of the recombining particles is involved, and the important energy transfer collisions involve strong interactions of the third body with only one of the recombining particles. These simplifying features make the comparison of ion recombination rate constants with theoretical predictions particularly significant.

The energy transfer mechanism used to describe ion recombination is

$$A^+ + B^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (A^+B^-)^*$$

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

$$(A^+B^-) \longrightarrow \text{nuetrals}$$

Here $(A^+B^-)^*$ is a pair of unbound ions close enough so that upon collision of one ion with the neutral M, the ions lose enough relative energy to become bound and eventually neutralized. Application of the steady-state assumption shows that the overall third order rate constant in the low pressure limit is the product of the equilibrium constant for formation of unbound ion pairs k_1/k_2, and the bimolecular rate constant for deactivation k_3. In his treatment of ion recombination, Thomson[2] in effect assumed k_3 would be equal to the total bimolecular collision rate constant if the relative kinetic energy of the

interacting ions was significantly greater than the mean energy of the free ions. Thus Thomson argued that oppositely charged ions with a separation r such that $e^2/r \geq (3/2)\ kT$ was satisfied could be deactivated at the bimolecular collision rate, whereas those at a greater separation could not be deactivated at all. The consequent definition of a critical radius $r_c = (2/3)\ e^2/kT$ for ion pair formation makes it possible to calculate the ratio k_1/k_2, and thus the recombination rate.

Despite the obvious simplifications in Thomson's theory, it is remarkably consistent with the experimental results.[1,3] However, it has recently been shown[4] that a rigorous calculation of the critical radius r_c as a function of ion and neutral masses leads to values of the third order rate constant much smaller than those found by experiment. Furthermore, numerical calculations[5,6] of the ion recombination rate have demonstrated the lack of validity of the critical radius concept. A significant contribution to the overall recombination rate comes from ions which have a separation greater than r_c, and not all collisions with neutrals of ions separated by less than r_c lead to deactivation. Even more significant is Feibelman's demonstration[6] that once deactivated, an ion pair may frequently be redissociated by subsequent collisions. His calculation shows that the fate of an ion pair may not be determined until it has undergone more than ten collisions. This suggests that recombination should not be described in terms of a single deactivating collision, but rather as a collisionally induced "diffusion" of the ion pair in energy space.

The diffusional formulation of the recombination-dissociation process has been the subject of several publications.[7-10] In particular, Pitaevski[10] has treated the case of electron-ion recombination as catalyzed by the parent neutral atom. While this problem is formally similar to ion-ion recombination, considerable simplification is possible because of the great difference between the electron and ion masses. In contrast, recombining ions are commonly of comparable mass, while the neutral catalyst may be heavier, lighter, or approximately the same mass as the ions. In this paper we give an expression based on the diffusional formulation which holds for any ratio of ion and neutral masses. However, it is to be expected that this approach to the problem is most appropriate when the fractional change of the kinetic energy of the ions upon collision is small. For ions of comparable mass, this condition is satisfied only when the mass of the neutral is smaller than the mass of the lighter ion. The comparison of calculated and experimental rate constants for such cases shows encouraging agreement.

Pitaevski's solution of the Fokker-Planck equation leads to the following expression for the pseudo second order recombination rate constant of a system obeying Coulomb's law

$$kn = \left[(2\pi\mu_{12}kT)^{3/2}\int_{-\infty}^{0} e^{E/kT}\,\frac{dE}{B(E)}\right]^{-1}, \qquad (1)$$

where

$$B = \frac{\pi^3\sqrt{2}}{2}\,\frac{e^6\mu_{12}^{3/2}}{|E|^{5/2}}\left\langle\frac{d(\Delta E)^2}{dt}\right\rangle, \qquad (2)$$

n is the concentration of neutrals, E is the total realtive energy of the ion pair, μ_{12} is the reduced mass of the ions (particles 1 and 2) and $\langle d(\Delta E)^2/dt \rangle$ is the square of the change in relative energy of the ions per unit time averaged over all ion configurations and ion-neutral collisions. The other symbols have their usual meaning. The differential energy exchange rate can be written[11] as

$$\frac{d(\Delta E)^2}{dt} = 2\pi b db \; V(\Delta E)^2 \; \frac{d\Theta}{2\pi} \; N(v_3, \theta, \varphi) dv_3 d\theta d\varphi \qquad (3)$$

where b is the impact parameter for ion-neutral collisions, v_3, θ, and φ are the polar coordinates of the velocity of the neutral molecule (particle 3), N is the velocity distribution function of the neutral, and Θ is the angle between the fundamental plane containing the velocity vectors of the ion-neutral collision pair $\underset{\sim}{v}_2$ and $\underset{\sim}{v}_3$ and the orbital plane in which the relative velocity vector $\underset{\sim}{V}$ of particles 2 and 3 rotate due to the collision. To obtain the desired energy exchange rate, $(\Delta E)^2$ must be evaluated and Eq. (3) must be integrated over b, Θ, v_3, θ, and φ.

It is assumed that the collision between the ion and the neutral is impulsive, and thus that ΔE is the change in relative kinetic energy of the ions. Then the approximate evaluation of $(\Delta E)^2$ is relatively simple if the mass m_2 of the ion undergoing collision is much smaller than the masses of the neutral and "observing" ion, as in the electron-atomic ion recombination problem. The simplification occurs mainly because the magnitude

of the electron velocity in the laboratory system is left largely unchanged by the collision with the massive particle, even though the direction of the electron velocity may change substantially. When the colliding ion and neutral are of comparable mass, and have laboratory velocities of the same magnitude as that of the observing ion, the problem is more complicated.

Chandrasekkar[11] has evaluated $(\Delta E)^2$ and $\langle d(\Delta E)^2/dt \rangle$ for particles of arbitrary mass that interact with a Coulomb potential, and much of his treatment can be adapted to the present problem. Two modifications are necessary. First, the angular distribution for the ion-neutral scattering will be assumed to be isotropic in their center of mass coordinate system. The second, more important change is that ΔE must be evaluated by using a coordinate system whose origin moves with the observing ion, rather than by using the space-fixed coordinate system employed by Chandrasekhar. That is, ΔE is the change in the relative energy of particles 1 and 2.

To evaluate ΔE, we note that as seen from particle 1, the center of mass velocity $\underset{\sim}{V}_g$ and relative velocity $\underset{\sim}{V}$ of particles 2 and 3 are

$$\underset{\sim}{V}_g = (m_2\underset{\sim}{v}_2 + m_3\underset{\sim}{v}_3)/(m_2+m_3), \tag{4}$$

$$\underset{\sim}{V} = \underset{\sim}{v}_2 - \underset{\sim}{v}_3 , \tag{5}$$

if $\underset{\sim}{v}_2$ and $\underset{\sim}{v}_3$ are understood to be the velocities of particles 2 and 3 <u>relative</u> to particle 1. The kinetic energy of particle 2 relative to particle 1 before the ion-neutral collision is

$(1/2)\mu_{12}v_2^2$, where μ_{12} is the reduced mass $m_1m_2/(m_1+m_2)$. If $\underset{\sim}{v}_2'$ is the relative velocity of the ions after the collision, we have

$$\Delta E = \mu_{12}(m_3/M_{23})\ V_g V(\cos\Phi' - \cos\Phi), \tag{6}$$

$$M_{23} = m_2 + m_3$$

where Φ and Φ' are the angles between $\underset{\sim}{V}_g$ and $\underset{\sim}{V}$ before and after the collision respectively. This expression differs from Chandrasekhar's only in that μ_{12} has replaced m_2.

The expression for ΔE may be squared, inserted in Eq. (3), and manipulations of the angular factors that are given explicitly by Chandrasehkar performed. Integration over the inclination of the oribtal plane Θ and over all impact parameters under the assumption of isotropic ion-neutral scattering leads to

$$\frac{d(\Delta E)^2}{dt} = 8\pi(\mu_{12}m_3/M_{23})^2 d^2 V_g^2 V^3 [(1/24)\sin^2\Phi + (1/6)\cos^2\Phi] N dv_3 d\theta d\varphi \tag{7}$$

where d is the hard sphere diameter.

The functions of the angle Φ in Eq. (7) can be expressed in terms of v_2 and v_3 by

$$V_g^2 V^2 \cos^2\Phi = M_{23}^{-2}[m_2 v_2^2 - m_3 v_3^2 + v_2 v_3 (m_3 - m_2)\cos\theta]^2$$

$$V_g^2 V^2 \sin^2\Phi = v_2^2 v_3^2 \sin^2\theta$$

where θ is the angle between $\underset{\sim}{v}_2$ and $\underset{\sim}{v}_3$. The term in $\cos\theta$ can be eliminated by use of

$$V^2 = v_3^2 + v_2^2 - 2v_2v_3 \cos\theta$$

In addition we will replace the distribution N by

$$N = N' \sin\theta/4\pi$$

where

$$N'dv_3 = n4\pi(\mu_{13}/2\pi kT)^{3/2}\exp-(\mu_{13}v_3^2/2kT)v_3^2dv_3$$

in which n is the concentration of neutrals, and μ_{13} is the reduced mass of particles 1 and 3.

Finally, in Eq. (7) we will substitute for d^2 the square of the maximum impact parameter for close collisions of particles which interact by the ion-induced dipole potential. Thus we write

$$d^2 = \gamma/V$$

$$\gamma = 2(\alpha e^2/\mu_{23})^{1/2}$$

where α is the polarizability of the neutral, e is fundamental charge, and μ_{23} is the reduced mass of the colliding ion and neutral. While this step may seem inconsistent with our earlier assumption of isotropic ion-neutral scattering, it is only a modest approximation. Collisions in which the impact parameter is less than the critical value $(\gamma/V)^{1/2}$ will involve deflections from the repulsive wall of the real potential, and this will give approximately isotropic scattering.

Making the foregoing substitutions in Eq. (7) we obtain

$$\frac{d(\Delta E)^2}{dt} = (\pi/3)(\mu_{12}m_3/M_{23})^2\gamma\left\{M_{23}^{-2}[(m_2-m_3)V^2 + (m_2+m_3)(v_2^2-v_3^2)]^2\right.$$

$$\left. + v_2^2v_3^2 \sin^2\theta\right\}N'\sin\theta d\theta(d\varphi/4\pi)dv_3 \qquad (8)$$

Integration over φ and of the second term in brackets over θ can be done immediately. To integrate the first bracketed term we use

$$VdV = v_2v_3 \sin\theta d\theta$$

and replace the integration over θ with an integration over V. Integrating from $|v_2-v_3|$ to $|v_2+v_3|$ then gives

$$\frac{d(\Delta E)^2}{dt} = \pi/6(\mu_{12}m_3/M_{23})^2\gamma\left\{8(m_2/m_{23})^2v_2^4 + 8(m_3/M_{23})^2v_3^4\right.$$

$$\left. + v_2^2v_3^2[(20/3)(m_2-m_3)^2/M_{23}^2 - 8/3]\right\}N'dv_3$$

Integrating over v_3 and averaging v_2 over[10]

$$f(v_2)dv_2 = (8\sqrt{2}|E|^{5/2}/\pi\mu_{12}^{9/2})(\tfrac{1}{2}\mu_{12}v_2^2 + |E|)^{-4}v_2^2dv_2$$

gives

$$\left\langle\frac{d(\Delta E)^2}{dt}\right\rangle = (4\pi/3)(\mu_{12}m_3/M_{23})^2\gamma\left\{4\left(\frac{m_2}{M_{23}}\right)^2\frac{|E|^2}{\mu_{12}^2} + 15\left(\frac{m_3}{M_{23}}\right)^2\left(\frac{kT}{\mu_{13}}\right)^2\right.$$

$$\left. + \frac{|E|\ kT}{\mu_{12}\mu_{13}}\left[5\left(\frac{m_2-m_3}{M_{23}}\right)^2-2\right]\right\} \qquad (9)$$

Equation (9) may be used in Eqs. (1) and (2) to evaluate the recombination rate constant. However, the final integration of Eq. (1) cannot be performed analytically for arbitrary values of the masses. While numerical integration for specified masses presents no difficulty, a convenient approximate expression for the rate constant can be obtained if Eq. (9) is made

homogeneous in $|E|$ by replacing $|E|^2$ and $(kT)^2$ by $|E|\ kT$. Insofar as the values of $|E|$ that make the most important contribution to the rate are approximately equal to kT, this modification is not a serious approximation. The rate constant derived in this manner is

$$k = (8\pi^2/9)(\alpha e^2/\mu_{23})^{1/2}\ (e^2/kT)^3(m_3/M_{23})^2 R \qquad (10)$$

$$R = \left\{4\left(\frac{m_2}{M_{23}}\right)^2 + 15\left(\frac{m_3}{M_{23}}\right)^2\left(\frac{\mu_{12}}{\mu_{13}}\right)^2 + \left(\frac{\mu_{12}}{\mu_{13}}\right)\left[5\left(\frac{m_2-m_3}{M_{23}}\right)^2 - 2\right]\right\}$$

The expression for the rate constant was obtained without making any explicit assumptions about the masses of the three particles. However, it is to be expected that the diffusional formulation of the recombination rate constant is most likely to be valid when the energy change upon collision is small. To find the mass ratios that satisfy this condition we remove from Eq. (9) the collisional rate constant factor $\pi\gamma$ and write

$$(\Delta E)^2 \cong \frac{4}{3}|E|\,kT\left(\frac{m_3}{M_{23}}\right)^2\left\{4\left(\frac{m_2}{M_{23}}\right)^2 + 15\left(\frac{m_3}{M_{23}}\right)^2\left(\frac{\mu_{12}}{\mu_{13}}\right)^2 + \left(\frac{\mu_{12}}{\mu_{13}}\right)\left[5\left(\frac{m_2-m_3}{M_{23}}\right)^2 - 2\right]\right\}.$$

Under the condition $m_2 \ll m_3 \cong m_1$, this becomes

$$(\Delta E)^2 \cong 4|E|\ kT\ (m_2/m_3)\ (m_1 + m_3)/m_1$$

to first order in m_2/m_1. As expected this physical situation satisfies the small fractional energy change criterion. In the opposite case where $m_3 \ll m_2 \cong m_1$, we get

$$(\Delta E)^2 \cong 4|E|\ kT\ (m_3/m_2)\ m_1/(m_1 + m_2)$$

which shows the fractional energy change is small for this case also. It is important to note, however, that the condition $m_3 >> m_2$ does not insure a small fractional energy change if $m_2 \cong m_1$. These conditions give

$$(\Delta E)^2 \cong \frac{4}{3} |E| \; kT \left[15\left(\frac{m_2}{M_{12}}\right)^2 + 3\left(\frac{m_2}{M_{12}}\right)\right]$$

which is not small. Also, when all three masses are equal the fractional energy change is large. Consequently the diffusional formulation is likely to be valid only when either the third body or one of the ions is much lighter than the other two particles.

It is of interest to note that for $m_2 << m_1 = m_2$, Eq. (10) ?? becomes

3? where is m_3?

$$k = \frac{16}{3} \pi^2 \left(\frac{\alpha e^2}{\mu_{23}}\right)^{1/2} \left(\frac{e^2}{kT}\right)^3 \frac{m_2}{m_3}$$

to first order in m_2/m_3. The same result can be found from Pitaevski's approximate expression for $\langle d(\Delta E)^2/dt \rangle$ if his cross section is replaced by $\pi\gamma/V$.

Table I shows a comparison between the calculated and experimental recombination rates for the cases that satisfy the small energy change condition. The agreement between the calculated and experimental constants is very good for the $NO^+ - NO_2^-$ recombination at 300°K. The predictions of the diffusional theory are approximately a factor of three smaller than the experimental rate constants for the thallium halide systems. This discrepancy may represent a real defect of the

theory, or may be due to the uncertainty concerning the identity of the ions in these systems. If, in addition to the assumed Tl_2X^+ and TlX_2^-, appreciable amounts of atomic ions were present in the experiments, the measured recombination rates would be greater than the calculated rates. Atomic ions might have been present in important concentrations in the experiments with TlI, but it is less likely that they were present in the TlBr and TlCl systems. Thus for these cases at least the predictions are clearly too small. Nevertheless, the general numerical agreement between the calculated and measured rate constants seems quite satisfying particularly in view of the simplifying assumptions which were used to derive Eq. (10), and the absence of any adjusted parameters.

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Table I. Calculated and Experimental[a] Rate Constants.

System		Temp (°K)	$k_{exp} \times 10^{26}$ (cm^6/sec)	$k_{calc} \times 10^{26}$ (cm^6/sec)
Tl_2I^+, TlI_2^-	Xe	530	3.0	0.86
	Ar	530	1.3	0.39
Tl_2Br^+, $TlBr_2^-$	Xe	590	2.0	0.70
	Ar	590	1.1	0.40
Tl_2Cl^+, $TlBr_2^-$	Xe	610	1.8	0.87
	Ar	610	1.2	0.37
NO^+, NO_2^-	He	300	4.1	3.6
	Ne	300	10.4	8.3
	H_2	300	5.8	5.6
	D_2	300	6.1	7.2

a. Data from Refs. 1 and 3.

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