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Calculations of ion-ion recombination rates at high pressures

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The classical theory of ion-ion recombination in gases of high density is extended to allow for arbitrary ratios of the masses of the three species involved. Calculations are performed for the recombination of Ar^+, Ar_2^+, Kr^+, and Kr_2^+ ions with F^- and of Hg^+ and Ar^+ with Cl^- in an argon gas. The effective two-body rates peak between 2×10^{-6} and 3×10^{-6} cm^3sec^{-1} at pressures above 1 atm.

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Three-body ion-ion recombination plays an important role in the kinetics of rare-gas—halide[1,2] and mercury-halide[3] lasers. However, there is little experimental or theoretical information on the rate of this process for the relevant ions. The purpose of this letter is to provide estimates of those rates.

A classical theory of ion-ion recombination at arbitrary gas pressures was developed by Natanson.[4] This method provides a way of connecting the low-density theory of Thomson and the high-density theory of Langevin, as is described in the book by McDaniel[5] and the review of Flannery.[3] We have modified the Natanson theory to allow the masses and collision properties of the positive and negative ions to be different.

The first step in the Thomson and Natanson theories is to define a trapping radius r_0 such that if an ion suffers a collision with a neutral atom while at a distance less than r_0 from an ion of opposite charge, the mean loss of kinetic energy would be so large that the ion pair cannot separate and recombination is likely. The second step is to calculate the rate at which ion pairs approach to within the distance r_0. This rate is enhanced by the attractive Coulomb interaction, but at high densities the approach is hindered by the neutral atoms and the rate is controlled by the mobilities of the ions. Finally, we calculate the probability that one of the ions suffers a collision while the ionic separation is less than r_0.

If we relax the assumption of Thomson and Natanson that the positive and negative ions have equal masses and collision rates, we must introduce two trapping radii, r_+ and r_-. Recombination is then assumed to occur if a positive ion undergoes a collision while the ion pair separation, r, is less than r_+ or if a negative ion suffers a collision while $r<r_-$.

In order to compute the trapping radius we consider the relative kinetic energy of an ion pair at a separation r. In a dilute gas this would be

$$T_{\rm rel}^{(0)}=\tfrac{3}{2}kT+e^2/r. \tag{1}$$

in which T is the ambient temperature. If one of the ions now collides with a neutral atom, this energy is reduced, on the average. If the cross section for ion-neutral collisions is isotropic in the center-of-mass frame, the mean relative energy becomes

$$T_{\rm rel}^{\pm}=\frac{3}{2}kT+\left(\frac{2\gamma_\pm-5}{\gamma_\pm-1}\right)\frac{e^2}{2r}, \tag{2}$$

where

$$\gamma_\pm=1+\frac{3}{4}\frac{(m_++m_-)^2(m_\pm+m_0)^2}{m_0m_+m(m_0+m+m_-)} \tag{3}$$

and m_0, m_+, and m_- are the masses of the neutral atom, the positive ion, and the negative ion. In this expression the upper (lower) signs are used if the positive (negative) ion suffers the collision with the neutral atom. This result does not reduce to that of Natanson in the equal-mass case because of an apparent inconsistency in Natanson's assumption of isotropic scattering in both laboratory and center-of-mass coordinates.

Thomson assumed that the ions are trapped if the kinetic energy given by Eq. (2) is insufficient to allow the ions to separate completely, i.e., is less than e^2/r. However, since it is possible for the ions to gain energy in subsequent collisions, Natanson modified this condition and required that the energy is insufficient for separation to a distance $r_0+\beta\lambda$, where λ is the mean free path and β is a parameter of the order of unity. We will use Natanson's criterion but with λ replaced by $\lambda_<$, which is the smaller of the mean free paths for the two ion species.

We then find that

$$r_\pm=\tfrac{1}{2}\beta\lambda_<\{[1+4e^2/kT\beta\lambda_<(\gamma_\pm-1)]^{1/2}-1\}. \tag{4}$$

Let us now denote the smaller and larger of r_+ and r_- by r_1 and r_2, respectively, and let us indicate the corresponding values of γ and λ by using the suffixes 1 and 2.

We now write two expressions for the flow of ion pairs toward one another, for ionic separations greater than r_2. From diffusion theory this flux can be written

$$I=4\pi r^2(K_-+K_+)\left(\frac{kT}{e}\frac{dn(r)}{dr}+\frac{e}{r^2}n(r)\right) \tag{5}$$

in which K_- and K_+ are the mobilities of the ions, e is the electronic charge, and $n(r)$ is the number of ionic pairs at a distance r. Second, using kinetic theory, we can equate this flux with the rate at which recombination

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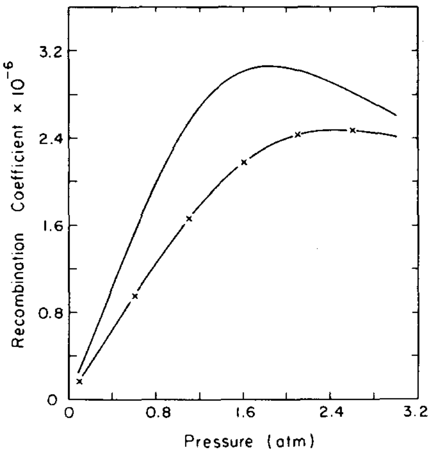

FIG. 1. Recombination rate in units of $cm^3 sec^{-1}$ for Ar^+ and Ar_2^+ ions with F^- in Ar as a function of the argon gas pressure;—Ar^+; ×—×: Ar_2^+.

is occurring for $r < r_2$. In the usual manner this is written

$$I = w\pi r_2^2 \bar{v} \gamma_2 n(r_2 + \lambda_<). \tag{6}$$

Here w is the probability of recombination for a pair of ions that approach within a separation r_2, and the remaining factors represent the rate of approach of such pairs.[4–6] The symbol $\bar{v}$ represents the average relative speed of the two ions and is assumed to be $(8kT/\pi\mu)^{1/2}$ where μ is the reduced mass of the ion pair.

In calculating w, we must allow for the collisions of one ion that occur for $r < r_2$, and the collisions of the other ion for $r < r_1$, and avoid double counting when both ions suffer collisions. We also take account of the curvature of the ionic trajectories and the variation in $n(r)$. In terms of Thomson's function

$$w_T(x) = 1 - (1/2x^2)[1 - \exp(-2x)(1 + 2x)] \tag{7}$$

we take

$$w = w_T(r_2/\lambda_2) + \rho w_T(r_1/\lambda_1)[1 - w_T(r_2/\lambda_2)] \tag{8}$$

with

$$\rho = r_1^2 \gamma_1 C_1 / r_2^2 \gamma_2 C_2$$

and

$$C_i = \exp[(\gamma_i - 1) r_i / \beta \lambda_<].$$

The ion-pair density $n(r)$ can now be obtained by integrating Eq. (5) and comparing with Eq. (6), leading to an effective two-body recombination coefficient

$$\alpha = \frac{I}{n(\infty)}$$

$$= \pi r_2^2 \bar{v} w \gamma_2 C_2 [1 + r_2^2 \bar{v} w \gamma_2 (C_2 - 1)/4e(K_+ + K_-)]^{-1}. \tag{9}$$

One of the advantages of this particular generalization of Natanson's theory is that it preserves the high-density Langevin limit. It does not allow for mutual neutralization in binary collisions. However, if the rate for that process were known, it could easily be incorporated in the manner suggested by Flannery.[6] Also the

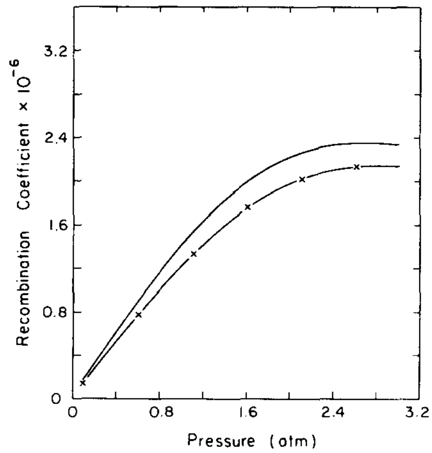

FIG. 2. Recombination rates for Kr^+ and Kr_2^+ with F^- in Ar;—: Kr^+; ×—×: Kr_2^+.

alternative Bates-Flannery theory of the low-density limit could be included.

The theory outlined above has been applied to calculate the rate of recombination of Ar^+, Ar_2^+, Kr^+, and Kr_2^+ with F^- and for Ar^+ and Hg^+ with Cl^-, all in argon gas at pressures between 0.1 and 3 atm. The mobilities were taken from the measurements by Dotan and Albritton[7] (F^- and Cl^-), McAfee *et al.*[8] (Kr^+), Beaty[9] (Ar^+ and Ar_2^+), and Chanin and Biondi[10] (Hg^+), or computed from the Langevin theory (Kr_2^+). The mean free paths were chosen to be consistent with the mobility data. The parameter β was taken to be unity in these calculations, and the temperature was assumed to be 300 °K.

The results, shown in Figs. 1–3, seem to indicate a systematic trend. For $Cl^- + Ar^+$ in Ar the masses are almost equal and the rate peaks at a value of $\sim 2.7 \times 10^{-6}$ $cm^3 sec^{-1}$ at about 1.9 atm. The larger masses of the other positive ions lead to smaller peak values occurring at higher pressures, whereas the smaller mass of F^- leads to a larger rate.

The major deficiencies in this approach are that no account is made for quantum effects and that no infor-

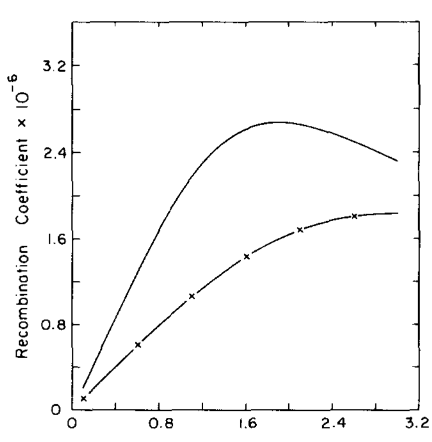

FIG. 3. Recombination rates for Ar^+ and Hg^+ with Cl^- in Ar;—: Ar^+; ×—×: Hg^+.

mation is gained about the neutral products. Also this method involves several arbitrary decisions, such as the choice of the parameter β. Improved calculations are underway to check some of the assumptions of the technique.

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