The recombination or combination time in expressions for volume recombination and combination of air ions and other aerosol particles

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(Manuscript received October 8, 1965)

ABSTRACT

A simple relationship, $1/\eta = 1/\eta_{BF} + 1/\eta_G$, exists between η, a general expression for volume recombination or combination coefficients, and its particular expressions, η_{BF}, in the diffusion-mobility approach (as by BRICARD and FUCHS), and η_G, when the central forces acting between the particles to be combined are taken into account (as by GUNN). The reciprocal combination coefficient $1/\eta$ may be regarded as a combination or encountering time θ. For the concentrations $[i] = [k] = 1$ cm^{-3}, the reciprocal recombination or combination coefficient for two species of particles (i and k) is $1/\eta = dt/-d[i] = dt/-d[k]$. For $d[i] = d[k] = -1$ cm^{-3}, $1/\eta = \theta$ is the recombination or combination time for two particles to be combined at unit concentrations. $\theta = \theta_D + \theta_\Delta$, where θ_D is the time for the diffusion-mobility stage, and θ_Δ is the time for the stage in the closest spacing between the particles, where the undisturbed diffusion-mobility treatment is not more valid. Using these time periods, it can be shown that

$$\eta = 1/\theta = 1/(\theta_D + \theta_\Delta) = 1/(1/\eta_{BF} + 1/\eta_G).$$

Almost all the previously known expressions for the volume recombination or combination coefficients of air ions and other aerosol particles at atmospheric pressure can be derived as particular cases of a general formula, the steps in the derivation of which have been demonstrated by SIKSNA, 1963, 1964*a*, 1964*b*. For pressures below and above that of the atmosphere, the problem is more complicated, as has been indicated by SIKSNA, 1964*b*, and this case will not be treated here. The volume recombination or combination appears when the concentration of the particles under consideration is statistically homogeneous in the whole volume.

At atmospheric pressure the general formula for the volume recombination or combination coefficients (in a form similar that used by NATANSON, 1959, and BRICARD, 1962) is as follows:

$$\eta = \frac{\pi R^2 P \langle v \rangle \exp\left\{-[\Psi(R+\Delta)]/kT\right\}}{1 + \frac{\langle v \rangle}{4D} \cdot \frac{R^2 P}{R+\Delta} \exp\left[-\frac{\Psi(R+\Delta)}{kT}\right] \int_0^1 \exp \frac{\Psi[(R+\Delta)/x]}{kT}\, dx}, \tag{1}$$

where η is the recombination or combination coefficient; $R = R_i + R_k$, where R_i and R_k are the radii of the particles; $\langle v \rangle = \sqrt{\langle v_i \rangle^2 + \langle v_k \rangle^2}$, where $\langle v_i \rangle$ and $\langle v_k \rangle$ are the mean thermal velocities of the particles; $D = D_i + D_k$, where D_i and D_k are the diffusion coefficients; Δ is the correction term of a boundary for the validity of the diffusion-mobility differential equation; Ψ is the electrical potential or potential energy when electrical forces are acting between the particles; P is the factor characterizing the enhancement of the capturing cross-section due to the central attraction forces acting between the charged particles and curving the linear trajectories near the target particle; k is the Boltzmann constant; and T is the absolute temperature.

As may be seen, formula (1) is applicable when considering the recombination or combination process as a two-body problem for two species of particles (i and k).

However, the same expression can be used in

considering the recombination or combination as a three-body process (as for example, NATANSON, 1959, and FUCHS, 1963, 1964, have done), replacing R by $d = a\varepsilon^2/(kT)$, where d is the radius of Thomson's sphere of active attraction, ε is the elementary electric charge, and a is a numerical factor with the different values (1/3, 2/3, 5/12, 1/4) used by different authors.

Formula (1) can be transformed into a more convenient expression, in which the particular terms are more distinctly separated:

$$\eta = \frac{4\pi D(R+\Delta)}{\frac{4D(R+\Delta)}{\langle v\rangle R^2 P}\exp\frac{\Psi(R+\Delta)}{kT} + \int_0^1 \exp\left\{\frac{\Psi[(R+\Delta)/x]}{kT}\right\}dx}. \tag{2}$$

Formula (2) is similar in form, but not exactly equivalent in content to an expression used by FUCHS, 1963, 1964, for the coefficient of combination of ions with other aerosol particles.

Very simple relationships may be obtained by introducing into (1) or (2) expressions for some particular combination coefficients:

$$\eta_{BF} = 4\pi D(R+\Delta)\Big/\int_0^1 \exp\left\{\frac{\Psi[(R+\Delta)/x]}{kT}\right\}dx, \tag{3}$$

which is a generalized expression of some formulas already used by BRICARD, 1949, and by FUCHS, 1955, and in the generalized form (3) shown by SIKSNA, 1963.

$$\eta_G = \pi R^2 P\langle v\rangle \exp\{-[\Psi(R+\Delta)]/kT\} \tag{4}$$

is a somewhat generalized formula given by GUNN, 1954. By applying these expressions in (1) or (2) we obtain:

$$\frac{1}{\eta} = \frac{1}{\eta_{BF}} + \frac{1}{\eta_G} \tag{5}$$

or

$$\eta = 1/(1/\eta_{BF} + 1/\eta_G). \tag{5a}$$

The reciprocal combination coefficient $1/\eta$ may be regarded as a combination or encountering time, i.e. a time interval $\theta = 1/\eta$ in seconds, after the passing of which it may be expected that an i-particle will be encountered or combined with a k-particle, when the concentration of particles of both species is 1 per ccm.

More detailed insight into this matter can be obtained by considering the definition of the combination coefficient given for two species of particles by the following equation of the rate of combination:

$$\frac{d[i]}{dt} = \frac{d[k]}{dt} = -\eta[i][k], \tag{6}$$

where $[i]$ and $[k]$ are the concentrations of the corresponding particles. From (6) the combination coefficient is

$$\eta = \frac{-d[i]}{dt}\cdot\frac{1}{[i][k]} = \frac{-d[k]}{dt}\cdot\frac{1}{[i][k]}\ [\mathrm{cm^3\ sec^{-1}}]. \tag{7}$$

In most cases the interpretation of this relationship is not considered and the expression is used formally, as, for example, by MCDANIEL, 1964, whose definition is as follows: "The recombination of two oppositely charged carriers is usually described in terms of their recombination coefficient α, which is defined as R, the number of recombination events per unit volume and unit time, divided by n^+n^-, the product of the number densities of the charge carriers. Thus $R = \alpha n^+ n^-$, where α is a positive quantity with cgs units of cm³/sec."

A somewhat similar formal interpretation is given by ISRAËL, 1957, in considering the dimension of the recombination coefficient of small ions: "The dimension (of the recombination coefficient) is cm³ sec⁻¹; this magnitude gives the number of occurrences (of recombination) (without dimension) per concentration (number per cm³) and per time (sec): $(1/\mathrm{cm^{-3}})\cdot\mathrm{sec^{-1}} = \mathrm{cm^3\ sec^{-1}}$."

It may be of some interest to transform (7) by using the expressions for the concentrations:

$$[i] = \frac{N_i}{V};\quad [k] = \frac{N_k}{V};$$

$$d[i] = \frac{dN_i}{V};\quad d[k] = \frac{dN_k}{V}, \tag{8}$$

where N_i and N_k are the numbers of the corresponding particles in the whole volume V. Thus

$$\eta = \frac{-dN_i}{N_i N_k}\cdot\frac{V}{dt} = \frac{-dN_k}{N_i N_k}\cdot\frac{V}{dt}\ [\mathrm{cm^3\ sec^{-1}}]. \tag{9}$$

By assuming that $V = 1$ cm³, $[i] = [k] = 1$ cm^{-3}, $N_i = N_k = 1$,

$$\eta = \frac{-dN_i}{dt} = \frac{-dN_k}{dt} [\text{cm}^3/\text{sec}]. \quad (10)$$

For unit concentrations the combination coefficient can be defined as the number of combination events $dN_i = dN_k$ per time period. Let us take $dt = 1$ sec. For $\eta = 10^{-6}$ cm³/sec, $dN_i = dN_k = 10^{-6}$, so that such an interpretation is also not of reasonable physical significance.

It seems more rational to use the reciprocal combination coefficient:

$$\frac{1}{\eta} = \frac{[i]\,[k]}{-d[i]} \cdot dt = \frac{[i]\,[k]}{-d[k]} \cdot dt\,[\text{sec}/\text{cm}^3] \quad (11)$$

or

$$\frac{1}{\eta} = \frac{N_i N_k}{-dN_i} \cdot \frac{dt}{V} = \frac{N_i N_k}{-dN_k} \cdot \frac{dt}{V} [\text{sec}/\text{cm}^3]. \quad (11\,a)$$

For unit concentrations $[i] = [k] = 1$ [cm^{-3}], and $V = 1$ [cm³], $N_i = N_k = 1$. In this case $d[i] = d[k] = -1$ [cm^{-3}], and $dN_i = dN_k = -1$, so that the reciprocal $1/\eta$ is the time period (interval) during which the combination takes place.

This time period or interval we can call the recombination or combination time for two particles (one i- and one k-particle) in 1 ccm at unit concentrations

$$1/\eta = \frac{dt}{V} = \theta\,[\text{sec}/\text{cm}^3]. \quad (12)$$

For $\eta = 10^{-6}$ [cm³/sec], $\theta = 10^6$ [sec/cm³], a reasonable magnitude for characterizing the combination process.

We now have the interpretation of the reciprocal combination coefficient $1/\eta = \theta$ as the combination time for two particles at unit concentrations and can introduce this time interval into (5). As has been shown, this time is split into two terms, $1/\eta_{BF}$ and $1/\eta_G$. When examining these terms in more detail, it can be seen that the first term describes the diffusion-mobility stage of the combination process and therefore it can be denoted as the diffusion-mobility term

$$1/\eta_{BF} = \theta_D. \quad (13)$$

On the other hand, the second term describes the stage of the combination process during which the central forces acting between the particles to be combined are working. This stage is started at a distance Δ from the target particle, so that this term can be written

$$1/\eta_G = \theta_\Delta. \quad (14)$$

The total combination time for unit concentrations is then

$$\theta = \theta_D + \theta_\Delta. \quad (15)$$

It is evident that relationship (15) has already been introduced by the derivation of the general formulas (1) and (2) when we divided the description of the movement of the particles to be combined into two stages—the diffusion-mobility stage and the stage in the closest spacing between the particles, where the undisturbed diffusion-mobility treatment is not more valid. In general formulas (1) and (2) this fact is not obviously shown, and the advantage of the present treatment, as in (13), (14) and (15), is that it shows this explicitly. In terms of the combination time the combination coefficient may be written as

$$\eta = \frac{1}{\theta} = \frac{1}{\theta_D + \theta_\Delta}. \quad (16)$$

Formulas (1), (2), (3) and (4) are generalized expressions, which must be adjusted for particular cases by inserting adequate values for the corresponding magnitudes and this task is not easy in all cases as shown by SIKSNA, 1964*a*. By using relationships (5), (13), (14), (15) and (16), this task may be facilitated.

Moreover, the general formulas used in this paper have not been canonized and may be improved or even replaced by other expressions. For this purpose, equations (5), (13), (14), (15) and (16) may also be useful, because the period of the combination time may be a simple sum of the time intervals for the different chosen stages of the combination process.

In conclusion, it may be asked whether in some cases the recombination or combination time would not be of more advantage in characterizing the recombination or combination processes than the recombination or combination coefficients used now.

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ВРЕМЯ РЕКОМБИНАЦИИ (СОЕДИНЕНИЯ) В ВЫРАЖЕНИИ ДЛЯ ОБЪЕМНОЙ РЕКОМБИНАЦИИ (СОЕДИНЕНИЯ) ИОНОВ ВОЗДУХА И ДРУГИХ АЭРОЗОЛЕЙ

Существует простая связь между объемным коэффициентом рекомбинации (соединения) h и его частными значениями h_{BF} и h_G. Здесь используется общее выражение для h; приближение диффузионной подвижности Bricard и Fuchs для h; а для h_G учитываются центральные силы, действующие между частицами при взаимодействии как у Gunn'a. Общий коэффициент $1/h$ можно рассматривать как время соединения или столкновения θ. Для концентраций $[i]=[k]=1$ см$^{-3}$ общий коэффициент $1/h$ для двух видов частиц (i и k) равен $1/h=dt/-d[i]=dt/-d[k]$. Для $d[i]=d[k]=-1$ см$^{-3}$ $1/h=\theta$ является временем рекомбинации (соединения) двух частиц, соединяющихся при равных концентрациях. $\theta=\theta_D+\theta_\Delta$ где θ_D — время состояния диффузионной подвижности, а θ_Δ — время, когда частицы находятся на ближайшем расстоянии друг от друга и невозмещенная диффузионная трактовка неверна. Используя эти времена, можно показать:

$$h=1/\theta=1/(\theta_D+\theta_B)=1(1/h_{BF}+1/h_G)$$