A NOTE ON THE CHANGE IN AVERAGE PARTICLE MASS DURING THE AGING OF AMMONIUM CHLORIDE SMOKES[1]

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An analysis of particle number and mass concentration data for the aging of ammonium chloride smoke in both still and moving air permits certain deductions concerning the average growth of particles under the experimental conditions used. With still air the average mass per particle increased for at least 5.5 hr., although the rate was smaller in the later stages; with rapidly moving air it increased for a comparatively short initial period and then decreased. The results are quantitatively described by equations involving two loss constants and the coagulation constant, whose values were determined experimentally (1).

In the attempt to obtain detailed information about the changes that occur with time in systems of solids dispersed in air, and about the influence of air motion on them, experiments have been performed on the aging of ammonium chloride smokes. This substance was chosen partly because of ease in handling certain experimental features, but also because it is expected to form a system in which the growth of particles is due primarily to coagulation on collision. The studies were concerned, not with the initial stages of formation of the aerosol, but with the period beginning at 3 min. after complete generation of the smoke (5 min. after the start of generation). Determinations of particle number (n, cc.$^{-1}$) and mass concentration (m, mg./m.^{3}) were made at 30-min. intervals for a period of 5.5 hr. For studies with moving air, a large pierced vane within the chamber was oscillated at a constant rate throughout the experiment. The reading of a non-directional thermocouple anemometer averaged over various positions in the 1.4 m.^{3} chamber was taken as an index of air motion (V, m./min.). A description of apparatus and techniques, and detailed data for n and m have been given previously (1).

It has been shown (1) that the variations of mass concentration and of particle number with time (t, min.) are described adequately by the relations

$$m = m_0 e^{-\alpha t} \tag{1}$$

and

$$\left(\frac{1}{n} + \frac{k}{\beta}\right) = \left(\frac{1}{n_0} + \frac{k}{\beta}\right) e^{\beta t} \tag{2}$$

under the conditions of these experiments, and that an expression of the form of equation 2 may be expected on general grounds when loss of particles to adjacent

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surfaces is appreciable and the particle size is not too small. In these equations α and β are "loss constants" and k denotes the coagulation constant; m_0 and n_0 denote, respectively, the values of m and n at the start of the observation period ($t = 0$). For "still" air α, β, and k were found to be 3.4×10^{-3} min.$^{-1}$, 3.2×10^{-3} min.$^{-1}$, and 2.2×10^{-8} cc./min., respectively. All three constants were increased by air motion, reaching respective values of 13.4×10^{-3} min.$^{-1}$, 9.8×10^{-3} min.$^{-1}$, and 5.4×10^{-8} cc./min. at an equivalent air flow of $V = 50$ m./min. The value of k for still air was not significantly higher than that expected from the Smoluchowski theory.

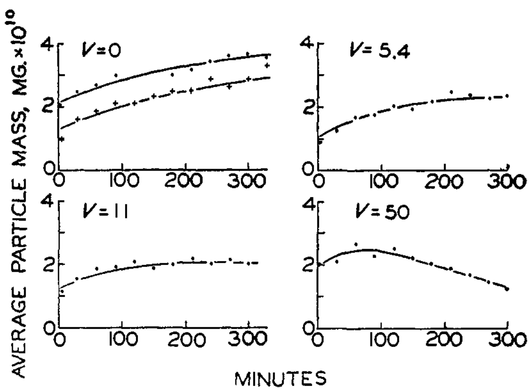

FIG. 1. Typical plots of average particle mass (ordinates, mg. $\times 10^{10}$) against time (abscissae, minutes) for air motion of 0, 5.4, 11, and 50 m. per minute. The points were calculated directly from observed n values and interpolation of determined m values. The curves were calculated from equation 7, using the following experimentally determined (1) constants:

V	μ_0	k	α	β
m./min.	*mg.* $\times 10^{10}$	*cc./min.* $\times 10^{8}$	*min.*$^{-1} \times 10^{3}$	*min.*$^{-1} \times 10^{3}$
0	2.16	2.1	3.2	3.0
0	1.24	2.3	3.6	3.3
5.4	1.08	2.8	6.2	5.5
11.	1.25	2.3	6.8	5.8
50.	1.88	5.8	14.	9.7

This note is concerned with a further consideration of the earlier data (1) in connection with the changes in average particle mass during the aging process.

THE GROWTH OF PARTICLES WITH TIME IN AMMONIUM CHLORIDE SMOKES

As has been shown previously (1) the rates of loss of mass, of particle number by collision with adjacent surfaces, and of particle number by coagulation, are described by the equations:

$$\frac{dm}{dt} = -\alpha m \tag{3}$$

$$\left(\frac{dn}{dt}\right)_l = -\beta n \tag{4}$$

$$\left(\frac{dn}{dt}\right)_c = -kn^2 \tag{5}$$

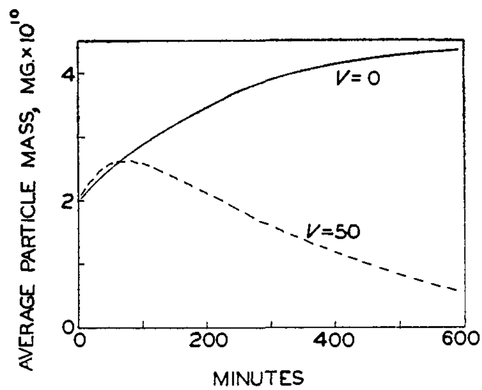

FIG. 2. Curves calculated from equation 7 for "average" smokes (m_0 = 50 mg./m.^{3}, $n_0 = 2.5 \times 10^5$ cc.$^{-1}$) with air motion of 0 and 50 m. per minute. The average values of previously determined (1) constants were used:

V	k	α	β
m./min.	*cc./min.* $\times 10^8$	*min.*$^{-1} \times 10^3$	*min.*$^{-1} \times 10^3$
0	2.2	3.4	3.2
50	5.4	13.4	9.8

Beyond 330 min. the curves are extrapolations.

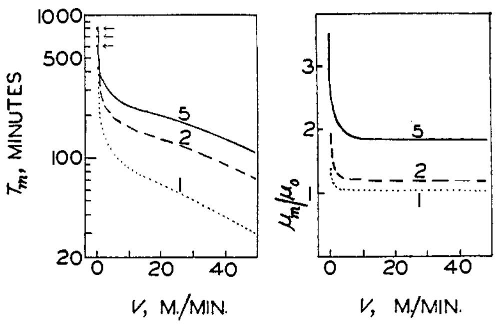

FIG. 3. The dependence on the degree of air motion of T_m and μ_m/μ_0 as calculated from equations 8 and 9. Mean values of the constants for various V values were taken from reference 1. The numbers attached to the curves indicate the n_0 values (cc.$^{-1}$ $\times 10^{-5}$).

Hence the average mass per particle in a hypothetical aerosol for which no surface loss occurs should increase linearly with time according to

$$\mu = \mu_0 + m_0kt \tag{6}$$

and should double in a time $T_2 = 1/n_0k$. Increase in the initial number of particles or in the degree of air motion (i.e., in k) would result in a corresponding decrease in T_2. On the other hand, in a hypothetical non-coagulating aerosol subject to surface loss the average mass per particle should decrease exponentially with time according to

$$\mu = \mu_0 e^{-(\alpha-\beta)t} \tag{6}$$

In the ammonium chloride smokes studied both coagulation and loss occurred, the two mechanisms tending to affect the average particle mass in opposite directions. It follows from equations 1 and 2 that

$$\mu = \frac{m}{n} = \mu_0 e^{-(\alpha-\beta)t} \cdot \left(1 + \frac{n_0 k}{\beta}(1 - e^{-\beta t})\right) \tag{7}$$

The closeness of fit of this expression with individual experimental data is indicated in figure 1 for various degrees of air motion. (In calculating the experimental points it was necessary to interpolate mass concentration data, since samples were not taken simultaneously with those for particle number determinations.) It is noteworthy that according to equation 7 the average mass per particle should reach a maximum value μ_m in a time T_m given respectively by

$$\mu_m = \mu_0 \frac{n_0 k}{\beta} \cdot \frac{\beta}{\alpha - \beta} \cdot e^{-\alpha T_m} \tag{8}$$

$$T_m = \frac{1}{\beta} \ln\left(\frac{n_0 k/\beta}{1 + n_0 k/\beta} \cdot \frac{\alpha}{\alpha - \beta}\right) \tag{9}$$

The trend toward this maximum is seen in the curves of figure 1, particularly in those for rapidly moving air.

The effect of air motion on the average particle mass during aging is illustrated by figure 2. The curves were calculated from equation 7, using average values for α, β, and k as previously determined (1). It is indicated that in rapidly moving air the average particle mass was considerably less than that in still air, except in the early stages of aging. This finding receives support from a comparison of the frequency distribution curves for apparent particle radius as previously obtained (1).

The dependence on air motion of the maximum value attained by the average particle mass and the time taken to attain it is illustrated in figure 3. The curves were calculated from equations 8 and 9, using average values of α, β, and k (1). The calculations represent some extrapolation of the original experimental data which covered a somewhat smaller range of initial particle number. Striking features are (*a*) the drastic reduction of T_m and μ_m by relatively slight air motion, and (*b*) the comparatively low value of μ_m attained.

REFERENCE

(1) LANGSTROTH, G. O., AND GILLESPIE, T.: Can. J. Research **B25**, 455 (1947).