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Studies of Salt Solution Aerosols. VIII.[1] The Effect of Humidity on the Stability of Spray-dried Na_2SO_4 Aerosol and an Estimate of the Particle Density

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The aerosols obtained by spraying an aqueous Na_2SO_4 solution of concentrations ranging from 0.1 to 10% by weight were dried by a furnace at 200 to 800°C and were then subjected to stirred aging at room temperature in an atmosphere of 90% relative humidity or less; the variations in both mass concentration and particle size were then measured with the lapse of time.

By employing the results thus obtained and by making some assumptions, the density of the particle in dried aerosols was calculated to be several tenths of one gram per cc, which is smaller by a factor of 3 to 4.5 than the bulk density of solid Na_2SO_4; further, the amount of water which the dried particle might hold if kept in a humidified atmosphere was estimated, with the finding that the density of a particle would decrease with increase in its water content; for example, the density of the particle with composition of $Na_2SO_4 \cdot 10H_2O$ would be 0.32 g/cc, smaller by a factor of 4 to 5 than the bulk density. In addition, the influence of water vapor on the stability of the dried aerosols was studied; it was found that the higher the humidity, the greater the rate of coagulation.

The production of the aerosols of hygroscopic salts and their properties in the presence of water vapor have been investigated by aerosol researchers, especially for the last two decades, from the viewpoint of meterological studies; in recent times, the spray-drying process has come into more frequent use by chemical engineers. The present paper will deal with the dehydration of aqueous Na_2SO_4 solution aerosols, the effect of the water vapor on the coagula-

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[1] Part VII: I. Sano and Y. Ueno, *J. Res. Assoc. Powder Tech.*, **8**, 94 (1971).

tion rate of the dried aerosols, and, further, the determination of the density of the dried particle.

A number of experiments have been performed in an attempt to determine the influence of such additions as water or some organic vapors upon the stability of aerosols, but the results have shown conflicting trends. For instance, Samokhvalov and Kozhukhova[2] describe that, for anmonium chloride aerosols, water or octyl alcohol vapor acts as a stabilizer, in contrast to the coagulation-promoting effect of water and butyric acid vapor observed by Smirnov and Solnseva.[3]

Concerning the density of an aerosol particle, it is usually assumed to be the same as that in bulk. This is valid for a homogeneous solid particle, but it might lead to erroneous results for an aggregate of solid particles formed by coagulation. It has been shown by Patterson and R. Whytlaw-Gray.[4] that the particles of cadmium, zinc, and magnesium oxides possess a loose or chain-like structure, so that it would be wrong to apply to them the normal bulk density in deducing their size from the rate of settling. After examining dried, microcrystallized particles of several inorganic salts, Duffie[5] has concluded that they are of density far less than normal. For the determination of the density of an aerosol particle, the ultramicroscope method might be used, but it has the disadvantages that reliable value of the settling velocity must be obtained by means of a large number of measurements and that the particles coarser than submicron-sized range can be managed only with difficulty unless a photographic device[6] is utilized; in the present paper, a different method has been adopted to determine the densities.

Experimental

Materials. The Na_2SO_4 used was of extra pure grade, and the H_2SO_4 of chemically pure grade.

Apparatus and Procedure. The mist generated by means of an atomizer of the glass-bead type[7] under a pressure of 2 kg/cm^2 was passed through an electric furnace and charged for 10 minutes into a plastic chamber of a volume of about 0.8 m^3 (1 m in height and 1.02 m in diameter), the inside of which had been kept saturated with water vapor by putting an aqueous H_2SO_4 solution on the bottom and by agitating the atmosphere over it. The aerosol in the chamber was continuously agitated during and after charging by constant-rate stirring (50 rev/min). The time of aging after charging was reckoned from the moment the charging stopped. The concentration of the dispersing solution was varied from 0.1 to 10% by weight, the temperature of the furnace, from 200° to 800°C, and the relative humidity, from 0 to 90%. The temperature in the chamber was held somewhere near 25°C throughout all the experiments. The humidity and the temperature were measured before and after each run by means of an electrical-type hygrometer and a glass set on the walls of the chamber. Table 1 shows the experimental conditions in condensed form.

Analyses of Mass Concentration and Particle Size. The technique of collecting the samples for the analyses has been described previously[9]; the concentration was determined through electrical-conductivity measurements of the solution obtained by dissolving into distilled water the Na_2SO_4 deposit in an electrical precipitator. As for the size, the dried aerosol that came out of the furnace to be aged in the chamber was introduced into a thermal precipitator, where the particles were gathered on electron-microscope collodion-mesh grids; the particles were viewed at a magnification of 2300X, 3000X, or 5000X and were found to be either isolated and rounded ones or chain-like aggregates. As the size of the former, the number-averaged diameter was taken, and while as that of the latter, the number average of the volume-equivalent diameters was taken.

Results and Discussion

Time Variations of Mass Concentration and Particle Size. From the experiment, it was found that the relative mass concentration decreases with the time and, further, that it decreases as the concentra-

TABLE 1. CONDITIONS USED IN THE EXPERIMENT

Run	Concentration of dispersing solution, %	Temperature of furnace, °C	Relative humidity in chamber, %	Temperature in chamber, °C
E_{10}	10.0	200	0	25.0
E_{15}	10.0	800	0	24.9
E_{20}	0.1	800	0	26.0
E_{21}	1.0	800	0	25.5
E_{22}	5.0	800	0	26.0
E_{23}	10.0	500	0	25.3
E_{24}	10.0	500	28.0	25.6
E_{26}	10.0	500	42.3	25.1
E_{28}	10.0	500	65.0	24.8
E_{33}	10.0	500	90.0[8]	25.9

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2) K. Samokhvalov and O. K. Kozhukhova, *J. Phys. Chem.* (*USSR*), **8**, 420 (1936).

3) L. A. Smirnov and V. H. Solnseva, *Colloid J.* (*USSR*), **4**, 401 (1938).

4) H. S. Patterson and R. Whytlaw-Gray, *Proc. Roy. Soc.* (*London*), **A113**, 302 (1927).

5) J. A. Duffie and W. R. Marshall, Jr., *Chem. Engr. Progr.*, **49**, 480 (1953).

6) V. D. Hopper and T. H. Laby, *Proc. Roy. Soc.* (*London*), **A178**, 243 (1941).

7) I. Sano and Y. Ueno, *Nippon Kagaku Zasshi*, **90**, 47 (1969).

8) It has been enough established experimentally that, in an atmosphere of which humidity is below 93%, there occurs no transition from solid phase to liquid one. *cf.* S. Twomey, *J. Appl. Phys.*, **24**, 1099 (1953).

9) Y. Ueno and I. Sano, This Bulletin, **44**, 908 (1971).

tion of the dispersing solution or the relative humidity of the chamber increases. Here, the relative mass concentration is defined as the ratio of the concentration (m_t) at time (t) to the initial one (m_0), determined by the extrapolation of m_t. It should be added that no influence of the temperature of the furnace upon the concentration change was found in so far an aqueous 10% solution was examined, the points corresponding to Runs E_{10}, E_{15}, and E_{23} overlapping one another.

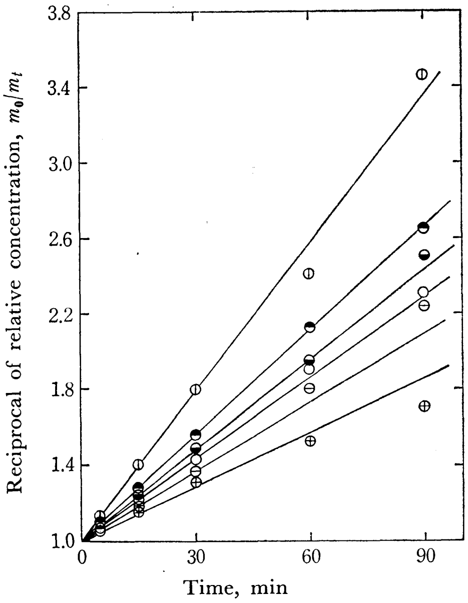

Fig. 1. Plot of the reciprocal of relative mass concentration against time.
⦶ E_{33} ◓ E_{28} ◒ E_{26} ○ E_{23} ⊖ E_{22} ⊕ E_{21}

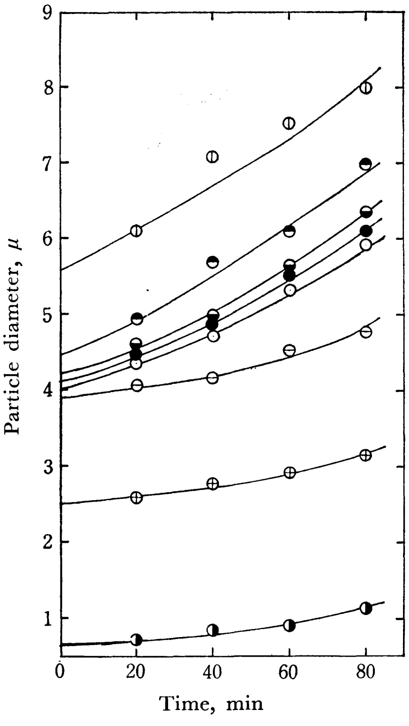

Fig. 2. Time variation of particle size under different conditions.
⦶ E_{33} ◓ E_{28} ◒ E_{26} ● E_{24} ○ E_{23} ⊖ E_{22} ⊕ E_{21} ◑ E_{20}

If the reciprocal of the relative mass concentration is plotted against the time, a linear relation is found for the early stage of the run (Fig. 1), suggesting that the time variation in the mass concentration is a second-order reaction.[9]

Figure 2 depicts the change in the particle size with the time under different conditions of the relative humidity in the chamber and of the concentration of the dispersing solution. From the figure, it is obvious that the particle size increases with the time and becomes larger with the increase in both humidity and concentration.

Estimate of the Density of Particle. The settling velocity of a particle of a monodisperse aerosol confined in a chamber under agitation may be expressed as follows[10]:

$$-\mathrm{d}n_t/\mathrm{d}t = n_t\cdot V_t/H \tag{1}$$

n_t: number concentration at time t
V_t: Stokes' velocity of settling at time t of a particle
H: height of chamber

The integration of Eq. (1) between time t to $t+\Delta t$ yields:

$$-\int_t^{t+\Delta t} \mathrm{d}n_t/n_t = 1/H\cdot\int_t^{t+\Delta t} V_t\,\mathrm{d}t \tag{2}$$

or

$$\ln n_{t+\Delta t}/n_t = -V_t/H\cdot\Delta t \tag{3}$$

V_t being assumed to be constant for a short interval of time, Δt. On substituting the relations:

$$n_{t+\Delta t} = 6\,m_{t+\Delta t}/\pi D_{t+\Delta t}^3\rho_{t+\Delta t} \tag{4}$$

$$n = 6\,m_t/\pi D_t^3\rho_t \tag{5}$$

m: mass concentration
D: diameter of particle
ρ: density of particle

it follows that:

$$-\ln\left[m_{t+\Delta t}/m_t\cdot(D_t/D_{t+\Delta t})^3\right] = V_t\cdot\Delta t/H - \ln\left[\rho_{t+\Delta t}/\rho_t\right] \tag{6}$$

Provided that the $\rho_{t+\Delta t}$ term is equal to ρ_t for the short interval Δt, the plot of the left-hand side of Eq. (6) against Δt passes through the point of origin, and the slope at the origin given the settling velocity at time, t, with the height of chamber H=100 cm. In Fig. 3, an example (Run E_{28}) is shown; the slope of the line gets steeper as the time becomes longer. For the other experiment runs, similar results are obtained. The values of the velocities thus found are represented in Fig. 4.

By equating the effective weight of particle at time, t, to the Stokes' drag, we obtain:

$$\pi/6\cdot D^3(\rho-\rho')g = 3\pi\eta VD \tag{7}$$[11]

where D is the diameter of the particle; ρ and V, its density and settling velocity; η and ρ, the viscosity and density of the medium (air), and g, the gravitational acceleration. By neglecting ρ' in comparison with ρ, we obtain:

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[10] D. Sinclair, "Handbook on Aerosols," Chap. 5, U. S. A. Atomic Energy Commission, Washington D. C. (1950).

[11] The subscript t is omitted for simplicity.

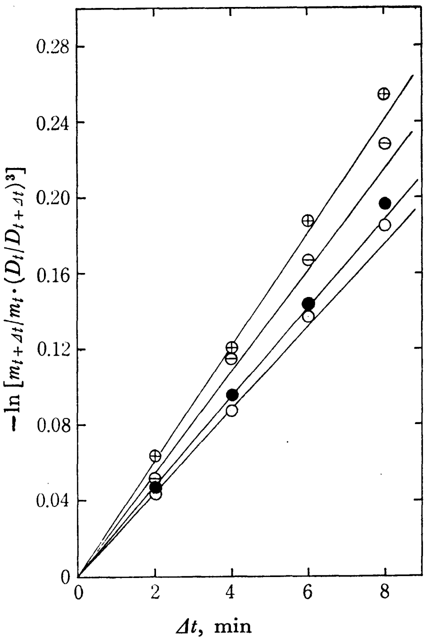

Fig. 3. Plots of Eq. (6) for Run E_{28}.
○ 20 min ● 40 min ⊖ 60 min ⊕ 80 min

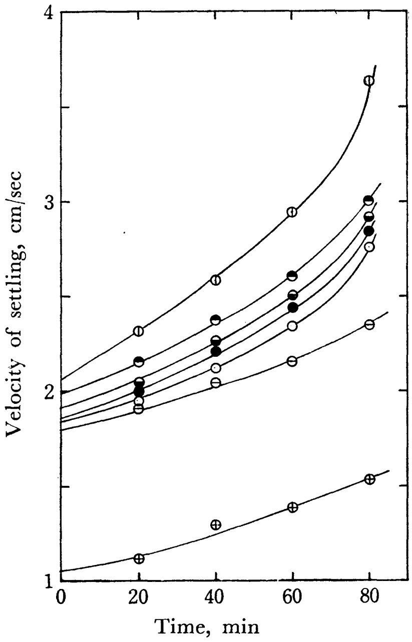

Fig. 4. Variation of the settling velocity of particles with time.
⦶ E_{33} ◓ E_{28} ◒ E_{26} ● E_{24} ○ E_{23} ⊖ E_{22} ⊕ E_{21}

$$\rho = 18\,\eta V/gD^2 \qquad (8)$$

From Eq. (8), the value of ρ at time t can be estimated if D and V at time t are known. The values obtained are given in Fig. 5; the points for Runs E_{10} and E_{15} are not shown, since they coincide with those of Run E_{23}. It may be seen in Fig. 5 that the density of the particle decreases with the time of aging and, further, with the increase in the humidity.

Effect of Humidity on the Coagulation Rate. The number concentration (n_t) at the time, t, is obtained by substituting m_t, D_t, and ρ_t (Fig. 5) into Eq. (5); the concentration at zero time (n_0) is determined by extrapolation to zero time of the plot of n_t against t. Figure 6 represents the plot of the relative number concentration (n_t/n_0) against the time; from the figure, it may be seen that the influence of water vapor is roughly linear with the humidity. The half-decay period in terms of number concentration and the particle size at that time are shown in Table 2; from the table, it may be seen that, as the humidity is increased, the half-decay period gets shorter, the particle size larger, and the particle density smaller. According to Duffie *et al.*[5], spray-dried Na_2SO_4 particles are hollow and crystallized, and they show holes with edges rounded inward and have thin, compact shells with radius/thickness ratios of the order of 10. The

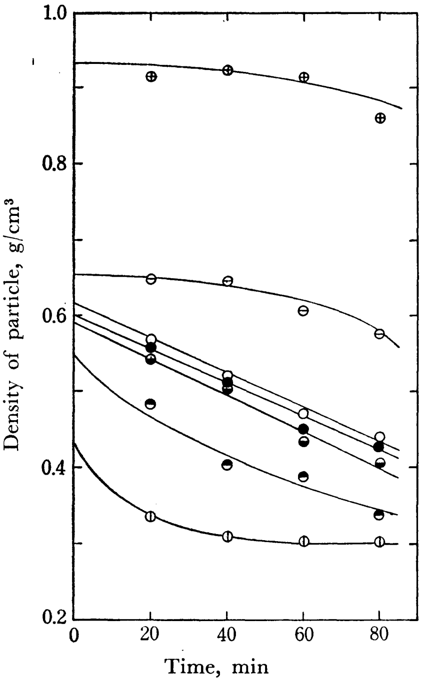

Fig. 5. Time-dependence of the density of air-borne Na_2SO_4 particles.
⊕ E_{21} ⊖ E_{22} ○ E_{23} ● E_{24} ◒ E_{26} ◓ E_{28} ⦶ E_{33}

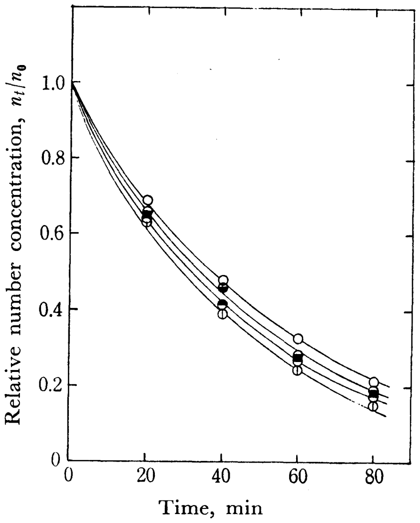

Fig. 6. Plots of n_t/n_0 against time.
○ E_{23} ◒ E_{26} ◓ E_{28} ⦶ E_{33}

Table 2. Particle diameter and density at the half-decay period

Run	Half-decay period, min	Particle diameter, μ	Particle density, g/cm^3
E_{23}	37	4.7 (4.0)	0.53 (0.62)
E_{26}	34	4.9 (4.3)	0.51 (0.57)
E_{28}	32	5.3 (4.5)	0.43 (0.53)
E_{33}	29	6.5 (5.6)	0.32 (0.43)

The parentheses express the value at zero time (Figs. 2 and 5).

Table 3. Dry particle-liquid droplet diameter ratio and the density of particle immediately after drying

Run	Concentration of dispersing soln, %	Furnace temperature, °C	Diameter of dry particle (d_s), μ	Particle-droplet diameter ratio, d_s/D_l	Density of dry particle (ρ_s), g/cc
E_{21}	1	800	2.5	0.22[15]	0.93[17]
E_{22}	5	800	3.9	0.43[15]	0.65[17]
E_{15}	10	800	4.0	0.56[15]	0.62[17]
E_{23}	10	500	4.0	0.56[15]	0.62[17]
S_{11}[16]	10	274	57.5	0.48	0.78
S_{13}[16]	10	167	64	0.49	0.78
S_8[16]	20	277	69	0.65	0.74
S_9[16]	20	164	74.5	0.67	0.74

formation of hollow particles due to the evaporation rate of water exceeding the diffusion rate of salt back into the inside, thereby creating internal voids after dryness is reached. In view of this fact, it might well be said that the Na_2SO_4 particles now under investigation are also so solidly-built that the particle size does not decrease in the presence of humidity. On the other hand, it was found by Andreasen *et al.*[12] that the particles smaller than 10 μ act as binders between colliding particles; further, Neumann[13] found that moisture leads to an increased stichness of the particles, particularly for hygroscopic ones.

Since the decrease in the relative mass concentration with the time follows the law of the second-order reaction rate (Fig. 1), whose mechanism will be discussed in a later paper, the decrease in the number concentration might be caused mainly by coagulation; some of the aggregates so formed fall to the bottom of chamber, vanishing from the system.

Comparison of the Density Found with Other Published Results. Crosby and Marshall,[14] after carrying out a series of experiment runs on spray-drying, at temperatures between 162° and 285°C, of aqueous Na_2SO_4 solutions with concentrations ranging from 10 to 20 wt%, concluded that, under all the conditions of temperature and concentration studied, the density of the particle increases as the size decreases, the variation being as great as fourfold; this explains, in part, why spraydried commercial products with small particles frequently exhibit higher densities than the corresponding products composed of large particles.

Table 3 presents comparison between the results obtained by the present authors and those obtained by Crosby and Marshall. It is apparent that two sets of figures are different from each other because of the difference in the experimental conditions, but that they are of the same order of magnitude. Concerning the variation in the density gets smaller with the time. This might be due to the formation of loose or chain-like aggregates by coagulation; the situation has been confirmed by the electron-microscope observation referred to above.

Determination of the Water Content of a Dried Particle. Let us suppose that droplets produced by atomization have passed through a furnace to be dried particles, without encountering mutual collision.

Since the solid content of a droplet will remain unaltered, there holds a mass-balance relation between the diameter (D_l) of a droplet produced by atomization and the diameter (d_s) of a particle formed by the dehydration of the droplet:

$$1/6\cdot\pi D_l^3\rho_l[1/(1+W_l)] = 1/6\cdot\pi d_s^3\rho_s[1/(1+W_s)] \tag{9}$$

ρ_l: density of liquid droplet

ρ_s: density of dried particle

W_l: water content of liquid droplet (grams of water per gram of Na_2SO_4)

W_s: water content of dried particle (grams of water per gram of Na_2SO_4)

Solving for the ratio of particle to droplet diameter, we obtain:

$$d_s/D_l = [\rho_l(1+W_s)/\rho_s(1+W_l)]^{1/3} \tag{10}$$

By the use of Eq. (10), the percentage of the water content of a dried particle or the number of H_2O molecules (X) associated with a Na_2SO_4 molecule can be estimated for Runs E_{24}, E_{26}, E_{28}, and E_{33}, all

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[12] A. H. M. Andreasen, N. Hofman-Bang, and N. H. Rasmussen, *Kolloid Zhur.*, **86**, 70 (1939).

[13] B. S. Neumann, "Flow Properties of Disperse System," Chap. X, ed. by J. J. Hermans (Leiden) 1953.

[14] E. J. Crosby and W. R. Marshall, Jr., *Chem. Eng. Progr.*, **54**, 56 (1958).

[15] Obtained from Eq. (10) by putting $W_s=0$. These runs have been conducted in dry atmosphere (Table 1).

[16] The symbol *S* is after Crosby *et al.*'s notation.

[17] Obtained from Fig. 5 by extrapolation to zero time.

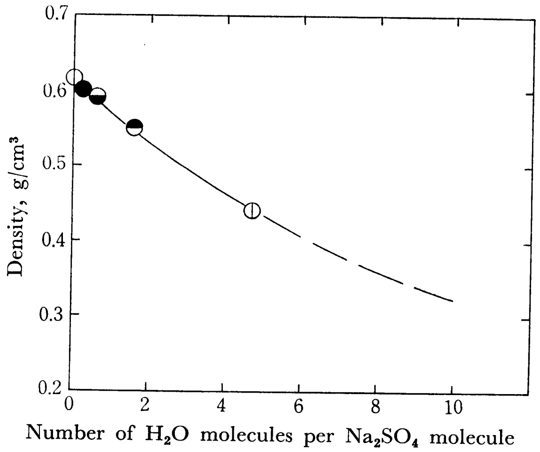

Fig. 7. Relation between density of the solid particle and its water content

○ E_{23} ● E_{24} ◒ E_{26} ◓ E_{28} ⦶ E_{33}

of which were carried out in a humidified atmosphere. The results are depicted in Fig. 7. The procedure is as follows. On assuming that the value of D_l $(7.3_2\,\mu)$ found with Run E_{23} (Table 3) is the same for these four runs, and, that dried particles leaving the furnace are hydrated in the humidified atmosphere to come to equilibrium with water vapor during charging, the W_s values are, first, calculated from Eq. (10) by substituting 7.3 for D_l, the values of d_s and ρ_s, being determined by extrapolation to zero time (Figs. 2 and 5). We know 1.089 for ρ_l and 9 for W_l: then, the W_s so found is converted into X. It may be seen in the figure that the particle density varies from 0.62 for an anhydrate particle to 0.32 for a decahydrate particles. These values are less than the normal densities, the ratio of normal density to that thus estimated being 4.4 for the former particle and 4.5 for the latter one. Futhermore, on the basis of the fact5) that hollow particles with a radius/thickness ratio of 10 are formed, the density of the shell can be calculated; the results are 2.3 for an anhydrate particle and 1.2 for a decahydrate one, values close to the normal densities of 2.7 and 1.4.