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STUDIES OF SALT SOLUTION AEROSOLS.XI.[1) THE COAGULATION RATE OF AN AQUEOUS SALT SOLUTION AEROSOL OF SODIUM SULFATE AND ITS APPLICATION TO THE ESTIMATE OF THE STABILITY OF AEROSOLS

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The coagulation rate of an aqueous salt solution aerosol of Na_2SO_4 has been determined in terms of number and mass concentration under various conditions, with the finding that the rate constant in mass concentration might be useful as a measure of coagulation rate. Some examples of its application are described in detail.

Rapid and spontaneous coagulation is one of the most striking characteristics of aerosols; the process goes on continuously so that aerosols become coarser and finally flocculate out. Coagulation rates have been investigated by different methods. The method measuring the decrease in number concentration is most available but requires elaborate techniques and troublesome operations. It has been shown with an aqueous salt solution aerosol of Na_2SO_4 2) that the result of experimental determination of the rate constant in terms of number concentration in "still air" was, if the loss to chamber surfaces was accounted for, in good agreement with the Smoluchowski's theoretical value.

It is known that, as for the factors affecting coagulation intrinsically or extrinsically, there may be vaporized organic substance as a surrounding atmosphere around the aerosol, in addition to Brownian motion, gravity, electric charge, temperature, pressure and so on. In this paper, firstly, the relation between the number and mass coagulation rate constants has been determined under various intensities of agitation. Experimentally, it is easier for aerosol investigators to measure the mass concentration than to count the particle number. It was found that the mass coagulation constant be taken as a measure of coagulation rate. Secondly, it has been shown that the mass coagulation rate of an aqueous salt solution aerosol of Na_2SO_4 changes in the presence of an organic vapor. Up to the present, no experiment has been performed of the effect of an organic vapor on an aqueous neutral salt solution aerosol. The organic vapors used in the experiment are divided into two groups: (a) vapors of nonpolar compounds such as carbon tetrachloride, benzene and toluene, and (b) those of polar compounds such as water, ethyl alcohol, acetic acid, ethyl acetate and acetone. Thirdly, the effect of humidity on

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the coagulation rate of the spray-dried solid aerosol of Na_2SO_4 has been investigated by measuring the mass concentration decrease.

Determination of the Coagulation Rates in Terms of Number and Mass Concentration of Aerosol under the Agitation of Atmosphere

The mist generated from an aqueous 10 % Na_2SO_4 solution under an atomizing pressure of 2 kg/cm^2 was charged for 10 minutes into a cylindrical chamber of 0.8 m^3 in volume and continuously agitated, during and after charging; the stirring was conducted at a rate of 30 rev/min during charging and at a scheduled rate during aging. Measurements of the number of air-borne particles in the chamber and of the particles deposited on the chamber surfaces were made, at frequent intervals for 3 hours of aging, by counting the number of the chemical spots impressed by particles on a reagent film.[3)] The total number of particles lost to the surfaces was estimated from the count by multiplying it into the ratio of the total area of the surfaces to the area scanned on the film. For the determination of the mass concentration, portions of mist were, periodically during aging, drawn with a constant rate air pump and passed through an electrical precipitator; the particles collected were dissolved in distilled water and the conductivity measurement was made.[4)] It was found that the mass concentration decreases with the lapse of time and markedly with the increase of agitation; the time was reckoned immediately after the charging of mist was stopped, and then the first film was exposed to the field of sedimentation of particles. It was found, further, that the decrease in number of air-borne particles with time gets more noticeable as the agitation is intensified and the same holds for the increase in surface loss, the greater part of deposition being due to sedimentation down to the bottom of the chamber while that to the top is negligibly small even at a rate of 250 rev/min.

From the data obtained, the coagulation constant in terms of number concentration, or the number coagulation constant and surface deposition one were derived by the graphical analysis of Gillespie et al.[2,5)] The total rate of disappearance of particles is given by

$$-dn/dt = \beta n + K_n n^2 \qquad (1)$$

where β denotes the deposition constant and K_n the number coagulation constant. On integrating Eq.(1), it follows that

$$\ln(1/n + K_n/\beta) = \beta t + K_n/\beta \qquad (2)$$

$$\ln(n) + \beta t = -K_n/\beta \cdot (\Delta n)_s + \ln(n_0) \qquad (3)$$

$$(\Delta n)_s = \beta \int_0^t n\,dt \qquad (4)$$

where n_0 is the number concentration at the start of run, n the number concentration at time t, and $(\Delta n)_s$ is cumulative number of particles lost to the surfaces from the start to time t, divided by the volume of chamber.

The surface loss $(\Delta n)_s$ was plotted against the value $\int_0^t n\,dt$ which could be calculated from the curve of the time variation of particle number; the slope of the straight line obtained gives the deposition constant β according to Eq.(4). The value of $\ln(n) + \beta t$ was plotted against $(\Delta n)_s$ and the coagulation constant K_n was determined from the linearity which was found, for "still air", to hold up to 90 minutes after the start of run and, as the agitation grew intense, was found to be limited in range. The value of K_n determined is shown in Table 1, where it is seen that the constant is affected by agitation; since the agitation leads to an increase both in the probability of the mutual collision between particles and in the chance of the surface deposition of particles, the constant will be expected to increase.

Determination of the Rate Constant in Mass Concentration under the Various Intensities of Agitation

Let us express the average fractional rate of mass concentration decrease in time t by ($C_0 - C_t$) / C_0 t ; this should decrease with the lapse of time,

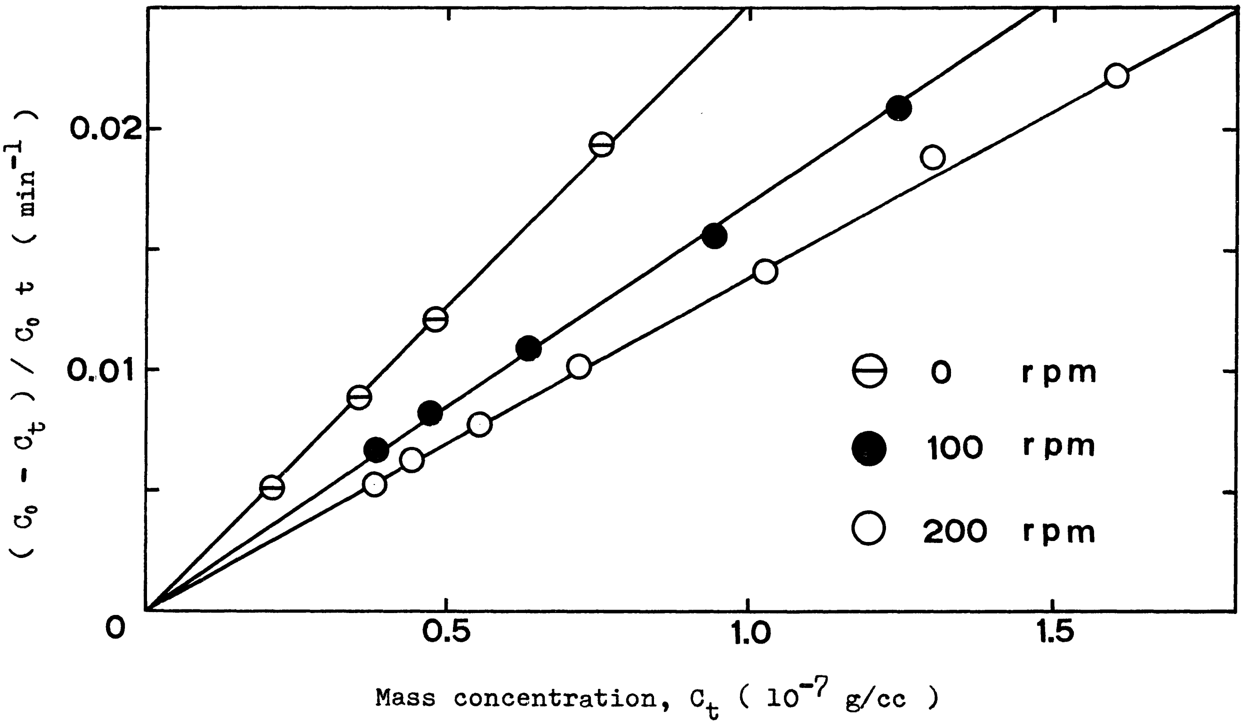

Fig. 1. Linear relationship between the average fractional rate and the mass concentration.

Table 1. Coagulation Rate Constants and Other Factors

Index of agitation (rev/min)	Coagulation constant and half-decay period K_n (10^{-8} cc.min^{-1})	K_m (10^5 cc.g^{-1}min^{-1})	$t_{1/2}$ (min)	Ratio of size at half-decay period of mass concentration
0	2.1	1.4	15.1	
50	2.5	1.5	14.1	1.0_3
100	2.9	1.7	12.4	1.1_0
150	3.6	1.9	11.1	1.1_6
200	4.6	2.5	8.4	1.3_0
250	6.3	2.9	7.3	1.4_3

if some of the particles coalesce as the result of mutual collision to vanish out of sight under sedimentation field. It was found that there holds a linear relation, as shown in Fig.1, between the average fractional rate and the mass concentration. Therefore,

$$(C_0 - C_t) / C_0 t = K_m C_t \qquad (5)$$

where K_m is a constant. Differentiating Eq.(5), it follows that

$$- d C_t = K_m C_t^2 \qquad (6)$$

which is of the form of second order rate equation, K_m corresponding to the rate constant in mass concentration. The fact that the rate of mass concentration decrease follows the rate law of second order reaction would be taken to suggest that the decrease in mass concentration of an aerosol is mainly controlled by coagulation. The value of K_m determined experimentally by means of Eq.(5) is recorded in Table 1; it is evident in the table that the two constants behave similarly, increasing in magnitude as the agitation becomes stronger. The last column of the table represents the ratio of the droplet size at half-decay period of mass concentration for the aerosol under the stirring of air to that in "still air"; it is apparent that the ratio varies in parallel with the two constants, though the variation is slight. It might well be concluded that the mass rate serves as a measure of coagulation rate.

Effect of Organic Vapors on the Stability of Aerosol

The aqueous salt solution mist of Na_2SO_4 produced in the same manner as in the above was continuously agitated at a rate of 200 rev/min in the presence of an organic vapor for one hour of aging. At frequent intervals, portions of the mist were drawn to collect the particles with an electrical precipitator and their mass concentrations were determined by conductivity measurement. At the same time, particle samplers were inserted into the chamber through a hole close to its bottom and the sizes of the particles gathered on their surfaces were determined by the chemical spot method which utilizes a reagent film.3)

It was found that there holds a linearity, as in Fig.1, between the average fractional rate and the mass concentration; the rate of mass concentration decrease follows the rate law of second order reaction in the atmosphere to which the various organic vapors are added. The rate constant K_m obtained is shown in Table 2. The ratio of the rate constant in the presence of an organic vapor to that in its absence might be considered as a measure of the stabilizing effect of the organic vapor. The ratio less than unity signifies stabilization.

The droplet sizes at half-decay period of mass concentration were examined in the presence of an organic vapor as well as in its absence and the ratio of the former to the latter is presented in Table 2. If the organic vapor used increases the stability of an aerosol, it will be expected for the ratio to be smaller than unity. It is seen in the table that there exists a clear correspondence between the stabilizing effect and the size ratio. Concerning the polar compounds, they dissolve easily into the solution and lowers its surface tension. It has been observed for an aqueous salt solution aerosol of NH_4Cl 6) that acetic acid vapor makes the aerosol unstable in contrast to the stabilizing effect now found for an aqueous salt solution aerosol of Na_2SO_4; the discrepancy

Table 2. Stabilizing Effect of Organic Vapors

Organic vapor	Concn. of vapor (m·mol/l)	K_m (10^5 cc·$g^{-1}min^{-1}$)	Stabilizing effect	Half-decay period (min)	Ratio of size at half-decay period
Na_2SO_4	0	2.5	——	8.4	——
Ethyl alcohol	0.22	1.8	0.72	11.7	0.91
	0.65	1.4	0.56	15.1	0.81
Acetic acid	0.11	1.7	0.68	12.4	0.88
	0.22	1.5	0.60	14.1	0.84
	0.34	1.4	0.56	15.1	0.81
Ethyl acetate	0.13	2.4	0.96	8.8	0.98
	0.26	2.0	0.80	10.6	0.95
Acetone	0.26	1.9	0.76	11.6	0.87
	0.52	1.4	0.56	15.1	0.81
Benzene	0.14	1.5	0.60	14.1	0.84
	0.34	1.3	0.52	16.2	0.80
Toluene	0.06	1.8	0.72	11.7	0.91
	0.11	1.6	0.64	13.2	0.86
Carbon tetrachloride	0.10	1.6	0.64	13.2	0.85
	0.20	1.4	0.56	15.1	0.82
	0.40	1.2	0.48	17.5	0.78

will come from the difference in the nature, acidic and neutral, of the salts used. As for the nonpolar compounds, they are sparingly soluble in the solution, but it is apparent in the table that their stabilizing effect is indisputable; the effect is reverse to that found with an aqueous salt solution aerosol of NH_4Cl.[6] The vapors of nonpolar compound might be adsorbed to the surface of particles and form a molecular layer thereon which prevents the coalescene of particles. Further, the layer would decrease the rate of evaporation[7] and, by conserving surface charges[9], would make the collisions between particles more elastic. The detailed mechanism on the stabilization of an aerosol caused by the addition of an organic vapor will be reported later.

Effect of Humidity on the Coagulation Rate of Solid Aerosol

The mist of an aqueous 10 % Na_2SO_4 solution generated under an atomizing pressure of 2 kg/cm² was passed through an electric furnace at 500°C and charged for 10 minutes into a chamber, inside of which had been kept saturated with water vapor by putting an aqueous H_2SO_4 solution on the bottom of the chamber and by agitating the atmosphere in the chamber. The aerosol was con-

Table 3. Effect of Humidity on Coagulation Rate of a Spray-dried Solid Aerosol of Na_2SO_4

Relative humidity (%)	K_m (10^5 $cc \cdot g^{-1} min^{-1}$)	Stabilizing effect	Half-decay period (min)	Ratio of size at half-decay period
0	0.91	——	70	——
28.0	0.95	1.0_4	65	1.0_1
42.3	0.97	1.0_7	62	1.0_3
65.0	1.1	1.2_1	54	1.0_7
90.0	1.5	1.4_3	38	1.2_2

tinuously agitated during and after charging by constant rate stirring (50 rev/min). The mass concentration was determined in a similar way as in the above. As for the size, the aerosol that had been subjected to aging in the chamber was introduced into a thermal precipitator, where the particles were gathered on collodion mesh grids, and the particles were viewed under electron microscope.

It was found that the rate of mass concentration decrease follows a process of second order reaction. On the other hand, the particle size increases with time and becomes larger with the increase in humidity. In Table 3, the effect of humidity on the stability of the aerosol is shown, together with the size ratio at half-decay period of mass concentration. It is evident from the table that humidity acts as a coagulation-promoting agent whose influence is represented by the mass coagulation rate constant (K_m).

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