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Highly Disperse Aerosols

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The properties of highly disperse aerosols of particle size ⩽100 Å are described, together with methods for their production and investigation. This class of aerosols, which has not hitherto been investigated systematically, is of great interest for the theory of the formation of condensation aerosols, the problem of atmospheric pollution and the fight against it, rocket technology, etc.

Special attention is paid to the theory of the formation of highly disperse aerosols, their coagulation, the diffusion method for determining particle size, the preparation of highly disperse materials via the aerosol state, i.e. questions to which the Reviewers have paid special attention in their publications. The bibliography contains 48 references.

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1. INTRODUCTION

In the present paper the term highly disperse aerosols (h.d.a.) is used in the sense of aerodisperse systems having a particle radius of around 10–100 Å, i.e. a Knudsen number (ratio of mean free path of gas molecules to particle radius $Kn = \lambda/r$) exceeding unity at atmospheric pressure. The most important property of h.d.a. must be that processes involving the transfer of momentum, energy, and mass from the particles to the medium and *vice versa* are described by the formulae of the kinetic theory of gases: i.e. the particles can be regarded simply as large gas molecules. Therefore the resistance of the gaseous medium to movement of the particles, the rate of their evaporation and of heat transfer to them, and also the rate of thermophoresis of the particles are proportional to the square of their radius. Since the apparent mean free path λ' of the particles themselves is $660\rho^{1/2}$ and $220\rho^{1/2}$ Å for those of radius 10 and 100 Å respectively, where ρ is the density of the particles[1], the "aerosol Knudsen number" λ'/r also exceeds unity in h.d.a.; therefore their rate of coagulation is more or less accurately represented by the well known formula for the number of collisions between gas molecules with $r \simeq 10$ Å, and approximately with $r \simeq 100$ Å, the rate of coagulation increasing with increase in particle size.

The vapour pressure of h.d.a. particles appreciably exceeds the normal vapour pressure of the material of the particles (by several 10% for $r \simeq 100$ Å and several times for $r \simeq 10$ Å). The scattering of light by the particles obeys Rayleigh's law accurately, while the intensity of the scattered light is so small that it is impossible to determine the particle size and concentration by macroscopic methods, and the particles are invisible in the ultramicroscope.

The Brownian motion of h.d.a. particles is so intense, while their inertia and rate of sedimentation under the influence of gravity are so small, that the deposition of h.d.a. on walls, streamlined obstacles, etc. occurs solely as a consequence of diffusion. The charge acquired by the particles in a bipolarly ionised atmosphere does not exceed 1 unit, the percentage of charged particles falling with decrease in their size.

In all the respects mentioned here, h.d.a. differ markedly from aerosols of particle radius ⩾ 0.1 μm, which have hitherto been the main subject of aerosol investigations. It is noteworthy also that, in view of the above fact concerning the charges on h.d.a. particles, their electrical mobility exceeds 0.001 V cm s^{-2}; thus the charged portion of atmospheric h.d.a. belongs, in the terminology of aerophysicists, to "intermediate" atmospheric ions.

2. FORMATION OF HIGHLY DISPERSE AEROSOLS

Although aerosols obtained by mechanical pulverisation or electrostatic sputtering of liquids and solids quite often contain very fine as well as coarse particles, relatively few of the former are formed, and their presence has little effect on the properties of such aerosols. The present h.d.a., in which all or most of the particles have the size indicated above, can be produced only by condensation. This is usually "physical" condensation of the supersaturated vapour of substances† having a very low vapour pressure at room temperature, the supersaturation being produced by rapidly cooling the vapour. This category includes also aerosols obtained in the spark, corona, and arc discharges, and by the explosion of wires. If, however, the supersaturated vapour is formed by a gaseous chemical reaction, condensation of the vapour is complicated by the fact that reaction takes place both in the gas phase and on the surface of already formed particles, the latter process quite often being catalytic in character and preponderating considerably over the former. Mention must be made also of "molecular" aerosols formed in certain chemical processes. Kogan[2] has shown that, in the photochemical decomposition of $Fe(CO)_5$ vapour under certain conditions, aerosols are formed whose particles consist of individual $Fe_2(CO)_9$ molecules. This is essentially $Fe_2(CO)_9$ vapour in a state of immense supersaturation, but possessing all the typical properties of aerosols; in particular, its particles may cause the condensation of supersaturated vapours of high-boiling liquids, i.e. act as "molecular condensation nuclei". Another analogous example is provided by "atomic" aerosols formed by the radioactive disintegration of emanations[3].

† We are concerned here, of course, with spontaneous condensation, since the concentrations of the particles thus formed exceed by several orders of magnitude the possible concentration of foreign condensation nuclei, including gaseous ions.

The size of particles formed by physical condensation depends primarily on the relative rates of formation of condensation nuclei and of their growth by the condensation of vapour on them. It follows from the modern theory of spontaneous condensation that the former rate increases far more rapidly than does the latter with increase in supersaturation of the vapour: i.e. finer particles should be obtained with increase in supersaturation. In fact, with the same initial concentration of the vapour and temperature of the vapour–gas mixture, rapidly cooled to room temperature, the degree of dispersion of the resulting aerosol is greater the less volatile the substance, i.e. the greater the supersaturation. This is shown especially clearly with compounds belonging to the same homologous series: increase in molecular weight produces a regular increase in the degree of dispersion of the aerosol.

On the other hand, the time during which supersaturation is produced, e.g. the rate of cooling of a mixture of vapour and gas, is of very great importance here. With slow cooling the degree of supersaturation actually remains slight throughout, since vapour is continuously removed from the system by condensing on already formed particles, foreign condensation nuclei, and the walls of the vessel; therefore coarsely disperse aerosols are formed. The more rapidly the system is cooled, the greater the actual supersaturation and degree of dispersion of the resulting aerosol.

The theoretical conclusion that the particle size of the aerosol diminishes with increase in the degree of supersaturation appears to contradict the firmly established fact that coarser aerosols are obtained with increase in the initial concentration of the vapour while the rate of cooling is maintained. Some part is played here by the increased evolution of heat of condensation that accompanies increase in concentration of the vapour, which tends to slow down cooling. However, the main reason is probably linked with the secondary process of coagulation of the particles. With the immense particle concentrations which are produced at the extremely large supersaturations necessary for the formation of h.d.a., the rate of coagulation is extraordinarily high. Let us suppose that the size or number of particles in condensation aerosols can be determined 0.1 s after their formation. Then it follows from the theory of coagulation that, with any initial particle concentration exceeding 10^{12} cm^{-3}, the concentration has fallen to about the same value of 2×10^{10} cm^{-3} at the instant of examination. The mean mass of particles formed by coagulation will clearly be proportional to the initial concentration of the vapour. In particular, if the vapour pressure of the substance at the temperature of condensation is extremely small, it may be assumed that all collisions between vapour molecules, between them and molecular aggregates, and also between these aggregates will result in their sticking together ("avalanche" condensation). In this case the mean mass of the particle aggregates will also increase with increase in concentration of the vapour.

Coagulation is accompanied by other significant processes in the particles of h.d.a. Quite often particles, which are initially spherical in shape and amorphous in structure, are gradually converted into small crystals even at low temperatures[4,5]. This ordering process takes place far more rapidly at high temperatures, in particular when the particles are heated by the electron beam in an electron microscope. Still more important changes take place in the structure of aggregates. In general, the coagulation of aerosols involves the formation of extremely loose aggregates, in which the area of contact between the particles is negligible, so that they are extremely unstable. In the first stage of condensation, however, when the temperature of the system is still high, the atoms (or ions) in the particles are highly mobile, and intense sintering and recrystallisation of the particles takes place in the aggregates. Coarse particles are known to sinter at temperatures above the "Tammann point" ($\sim 0.6\,T_m$, where T_m is the melting point on the absolute temperature scale), whereas in very fine particles sintering is already possible at considerably lower temperatures[6]. Particles in the form of liquid droplets (and very fine droplets can be extremely strongly supercooled) coalesce on contact.

In most cases coagulation which has begun at a high temperature continues as the system is cooled, so that both dense coalesced, sintered, or recrystallised "primary" aggregates and loose "secondary" aggregates can be formed (aggregates in certain carbon blacks, for example, possess such a structure).

It must be stressed that there is a fundamental difference between aerosols comprising individual particles having radii of the order of 10–100 Å and aerosols containing more or less coarse aggregates of such particles. Only the former possess the characteristic properties of h.d.a. mentioned at the beginning of the paper, but aggregation of the particles is unavoidable on their sedimentation, and the powdered deposits thus obtained from uncoagulated and from coagulated aerosols (the latter containing only loose aggregates) are practically indistinguishable in properties. Coagulated h.d.a. are also of interest in view of the great practical value of such highly disperse powders.

Cooling of a mixture of vapour and gas, with the formation of condensation aerosols, can proceed uniformly throughout the volume of the mixture (when it is expanded adiabatically) or else under non-uniform conditions, when the temperature and the supersaturation differ at different points in the system (when the mixture of vapour and gas is mixed with a cold gas or when it is cooled externally). It is very difficult to produce in a Wilson chamber the high supersaturations necessary for formation of h.d.a.; this is far more easily achieved in supersonic nozzles[7,8]. Unfortunately, the h.d.a. formed in them vaporise extraordinarily rapidly, and they can be investigated only by indirect methods[9,10].

The most important method of obtaining h.d.a. is by mixing. This is achieved most simply by heating a weighed portion of the substance in a closed vessel[11–13], when mixing occurs by means of convection currents, and formation of the aerosol is almost uncontrollable. Furthermore, the resulting aerosol cloud is fairly slowly diluted with a neutral gas, and as a result a strongly coagulated and extremely polydisperse aerosol is obtained. In a similar method—the preparation of h.d.a. by exploding a wire[14,15]—mixing occurs far sooner, but in this case, too, the process of mixing is uncontrolled. A better method, enabling aerosols to be obtained which are more highly disperse and uniform in particle size, is mixing in a flow.

There are two ways—in a mixer and in free space—in which such mixing can be accomplished. In the former case the processes of mixing and condensation take place in the mixer itself, a considerable portion of the vapour condensing on the walls of the mixer. This lowers substantially the yield of aerosol, but on the other hand it helps to maintain a constant degree of supersaturation in the mixer, and hence a constant concentration and degree of dispersion of the resulting aerosol, and it diminishes the harmful effects of fluctuations in temperature and concentration of vapour in the mixture with air. This "buffering" action of mixers is especially apparent when for-

eign condensation nuclei are introduced into a cold gas flow with the aim of obtaining more monodisperse aerosols: at low concentrations of the nuclei almost all the vapour condenses on the walls, the actual degree of supersaturation in the mixer being practically independent of the rate of condensation in space, and as a consequence the size of the resulting particles is independent of their concentration[16].

When streams of gases are mixed in free space, the whole of the vapour is converted into an aerosol. There is no necessity for two streams to be present: a free turbulent stream of a hot mixture of vapour and gas, escaping from a nozzle into a cold, stationary gas, mixes with the latter sufficiently rapidly for h.d.a. to be formed. This method is preferable for the preparation of large quantities of h.d.a., but it has been less studied than has the preceding method.

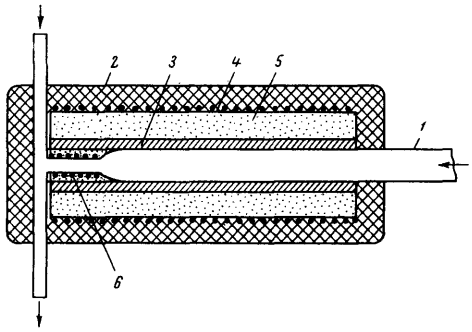


Figure 1. Generator for h.d.a.:
1) quartz tube; *2*) thermal insulation; *3*) steel tube; *4*) heating coil; *5*) ceramic tube; *6*) heating coil.

In the Laboratory for the Physics of Aerodisperse Systems at the Karpov Institute the formation of h.d.a. of sodium chloride has been studied by the method of mixing in a T-piece[17]. The generator illustrated in Fig. 1 was used. A quartz tube of diameter 20 mm, filled with ceramic rings coated with a layer of sodium chloride, was placed in an electric furnace operated with a stabilised voltage. The narrow part of the tube, which served as a superheater, was heated by a separate winding. In the steady state the temperature of the tube was maintained constant to 1 deg. The temperature profile along the axis of the tube shows that vaporisation of the salt took place under conditions of almost complete saturation with sodium chloride vapour of nitrogen flowing through the tube at a rate of 100–200 cm^3 min^{-1}. This is very significant, since work in which salt had been deposited as a thin layer on the surface of a nichrome coil had revealed a gradual fall in concentration of the vapour in the gas stream[18,19]; in this case the gas had obviously been far from saturated with the vapour, and recrystallisation of the salt on heating had caused a considerable decrease in the rate of evaporation.

The nitrogen and sodium chloride vapour leaving the tube were mixed in a T-piece with cold, filtered air flowing at a rate of 10–20 litres min^{-1}. In the absence of a superheater the vapour condensed completely on the walls of the mixer; with the superheater present, 90–99.9% of the vapour condensed on the walls depending on the experimental conditions. It was established by the method described on p. 860 that the h.d.a. obtained in this way were fairly monodisperse; the radius of the particles could vary from 7 to 50 Å, and the counted concentration from 10^2 to 10^7 cm^{-3}. The polydispersity of the h.d.a. increased appreciably at a radius of 50 Å. At the above concentrations the degree of coagulation of the h.d.a. was negligible. Both the size and the concentration of the particles increased with rise in the temperature of the furnace and with the rate of flow of nitrogen in it, i.e. with increase in the concentration of the h.d.a. by weight. A similar procedure was used to prepare h.d.a. from a series of alkali-metal halide salts.

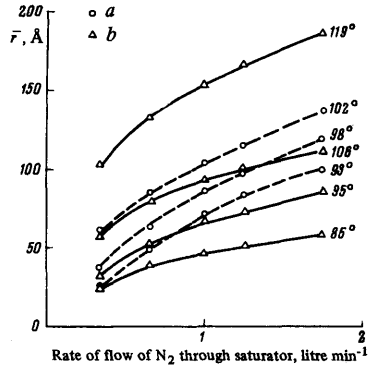


Figure 2. Dependence of mean particle size of dioctyl sebacate on conditions of operation of KUST apparatus, for air containing condensation nuclei (2×10^7 cm^{-3}) flowing at (litres min^{-1}): *a*) 11.0; *b*) 6.0. The temperature (°C) of the saturator are indicated on the curves.

Dioctyl sebacate h.d.a. have been prepared[20] by means of the KUST generator designed by Kogan and Burnasheva[16], in which the flows were mixed in a spray type of mixer: here a mixture of vapour and air escapes from a circular orifice, is mixed with a stream of cold air emerging from a concentric annular slit, and enters a diffuser. Condensation nuclei—the sodium chloride h.d.a. mentioned above, having $\bar{r}$ = 17 Å—were used to obtain more monodisperse aerosols. In this way aerosols of dioctyl sebacate were prepared having $\bar{r}$ between 30 and 300 Å. Fig. 2 shows that the particle size increases with rise in the temperature at which the nitrogen is saturated by dioctyl sebacate vapour and with increase in the rate of flow of nitrogen through the saturator, as with the sodium chloride h.d.a. discussed above. In the present case, however, the degree of dispersion of the h.d.a. could be controlled also by varying the concentration of condensation nuclei: with increase in the latter above a certain limit (see above) the particle size understandably diminished.

By mixing gas flows in mixers, h.d.a. can very conveniently be obtained with controllable properties and a fairly high degree of monodispersity, but this method is unsuitable for the accurate study of the formation of aerosols by

physical condensation, since in the present case the process is greatly complicated by the condensation of vapour on the walls of the mixer. This disadvantage is absent when free streams are mixed, a method by which h.d.a. have been obtained from several substances in the Laboratory for the Physics of Aerodisperse Systems. Since there are no losses of material in this case, the concentration by weight of the resulting aerosols was considerably higher than in mixers, and the aerosols were strongly coagulated. The particle size in the aggregates was therefore determined from the specific surface of the deposited h.d.a.

The formation of h.d.a. has been studied in the greatest detail from molybdenum trioxide[21] and from silver[22]. The generator used differed from the apparatus illustrated in Fig. 1 by the absence of the T-piece: the narrow portion of the quartz tube (the superheater) terminated in a circular orifice, from which a stream of the hot mixture of vapour and air escaped into cold air, the molybdenum trioxide being placed in a boat in the furnace. Here vaporisation did not occur under saturated conditions, and the concentration of vapour in the mixture could be controlled both by the temperature of the boat and by the rate of flow over it. The aerosol formed in the turbulent stream was sucked without loss into an electrostatic precipitator, where it settled out. The specific surface of the deposit was determined by the BET method, and thence the mean particle radius was calculated.

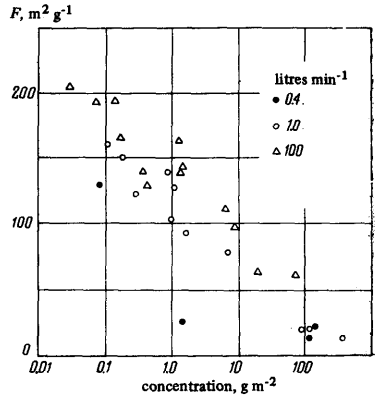


Figure 3. Dependence of specific surface of MoO_3 powders on concentration of vapour and rate of flow of air through producer (diameter of nozzle 2 mm, temperature at outlet from nozzle 820°C).

The content of molybdenum trioxide in the hot mixture of vapour and air is plotted as abscissa in Fig. 3, from which it is evident that the mean particle size in the aggregates increases with increase in concentration of the vapour. As already mentioned above, this is probably explained by coagulation of the aerosol at temperatures at which the particles in the aggregates coalesce or sinter. At low vapour concentrations the effect of coagulation is weaker, and the particle size is almost independent of concentration: the higher the latter, the stronger the influence of coagulation. The diminished particle size with increase in rate of flow is probably due to the accelerated dilution of the aerosol, so that it is less coagulated. In this case the effect of rate of flow will also clearly increase with vapour concentration.

Calculations on the formation of a silver aerosol, examination of electron micrographs of samples of the aerosol withdrawn at various stages in the process of formation, and investigation of the effect of heating on the specific surface of powders obtained by precipitating silver aerosols have shown that at vapour concentrations of 10^{14}–10^{16} mol. cm^{-3} coagulation plays a decisive part in producing the size distribution of the aerosol[22]. The final result is determined by the ability of the particles to coalesce and sinter on coagulation. As the aerosol cools, the coarse particles lose their ability to coalesce on collision, and merely sinter. This course of the process probably explains the spherical shape of the primary particles in certain aggregated aerosols of condensation origin, e.g. in carbon black aerosols. Other workers[13,23] have also concluded that coagulation, accompanied by coalescence of the particles, plays a decisive part in the formation of concentrated h.d.a.

A procedure analogous to that which has been described[21] has been used to obtain h.d.a. of bismuth molybdate, nickel chloride, and metallic silver. Allowing streams of argon containing the vapours of zinc, cadmium, bismuth, and tin(II) oxide to escape into air has yielded h.d.a. of the corresponding oxides and tin(IV) oxide having approximately the same particle size as with molybdenum trioxide, and in the case of tin dioxide $\bar{r} \simeq 15$ Å.

The preparation of h.d.a. by the decomposition of certain compounds in the plasma must also be included among processes in which aerosols are formed by the mixing of flows at different temperatures. As a consequence of the high temperatures reached in plasmas, the vapour formed by a chemical reaction probably becomes supersaturated only during cooling of the flow, and condensation is preceded by the chemical reaction. Examples of such processes are the preparation of carbon black by the decomposition of benzene vapour in the plasma, described by Sofronov[24], and the formation of nickel h.d.a.[25] by the decomposition of nickel pentacarbonyl.

3. DETERMINATION OF CONCENTRATION AND PARTICLE SIZE OF HIGHLY DISPERSE AEROSOLS

Only one method—enlarging the particles by condensing vapour on them—is in practice available for determining the number of particles in h.d.a. per unit volume. This method, which was proposed by Aitken as long ago as the nineteenth century, is based on the fact that condensation of a vapour on aerosol particles is possible at supersaturations which are insufficient for spontaneous condensation. Originally, water droplets formed by the adiabatic expansion of an aerosol containing water vapour were counted visually, but this method was too slow and laborious. At the present time, therefore, meteorologists employ photoelectric counters[26,27] to count "atmospheric condensation nuclei", these measuring the weakening or scattering of light by the aqueous mist formed on the adiabatic expansion of saturated air in the counter chamber. The counter is first calibrated by means of aerosols containing a known concentration of particles.

Use of the KUST apparatus mentioned above is considerably more convenient for laboratory investigations of h.d.a.[16] The test aerosol is mixed in a spray mixer with a gas flow containing the vapour of a high-boiling liquid, after which the concentration of droplets in the fairly monodisperse

fog formed is measured either visually or with a photoelectric particle counter. The great advantage of the KUST apparatus is that, at particle concentrations not exceeding 10^4 cm^{-3}, the size of the droplets formed by condensation no longer depends on the particle concentration. It is therefore sufficient to determine with a nephelometer the intensity of light scattered by the fog formed in the apparatus at one definite particle concentration in order to obtain the whole calibration graph (straight line). For relative nephelometric determinations of concentration, however, calibration is not required at all, since the nephelometer readings are proportional to the particle concentration.

To determine the absolute concentration of h.d.a. particles we had to ascertain the completeness of their "development" in the KUST[28]. For this purpose the particles were developed with an increasing degree of supersaturation of the vapour of the liquid developer (dibutyl phthalate). It was found that, in agreement with theory, there exists for each particle size a definite minimum supersaturation, at which all the particles are developed, further increase in the supersaturation (until spontaneous condensation begins) leading merely to enlargement of the fog droplets without change in their number. The minimum supersaturation necessary clearly increases with decrease in particle size. According to Kogan's hypothesis, liquids of extremely low vapour pressure, e.g. dioctyl sebacate, must be used to develop very fine particles; in this way he was able to develop "molecular" nuclei[2].

In view of the extremely large diffusion coefficient of particles having radii of around 10–30 Å, considerable losses of such particles from diffusion and thermophoresis to the walls were to be expected in the KUST apparatus. The design of the KUST mixer was therefore modified as shown in Fig. 4: the aerosol flows through the central orifice, while nitrogen containing superheated dibutyl phthalate vapour flows through the annular slit (the opposite to what occurs in the KUST apparatus). In this mixer the thermophoresis of particles preceding the mixing zone takes place from the walls towards the axis, and thus opposes the deposition of particles on the walls by diffusion.

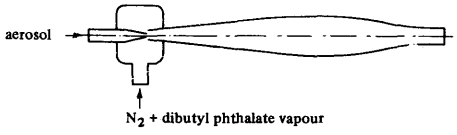


Figure 4. Mixer for developing aerosols.

Actually, the losses on the passage of an h.d.a. through a "blank" new mixer (i.e. in the absence of the vapour) were only 4% for $\bar{r}$ = 45 Å and 5.5% for $\bar{r}$ = 25 Å. Since these losses are caused by the diffusion of particles to the walls of the diffuser, the losses should be still smaller when the particles are enlarged by condensation. The fact that particles had sufficient time to be enlarged before they started to settle in the diffuser was established in special experiments.

In order to be able to utilise the above specific property of the KUST apparatus at concentrations exceeding 10^4 cm^{-3}, accurate dilution of h.d.a. was required. For this purpose an aerosol diluter was constructed[28], in which the deposition of h.d.a. by diffusion was insignificant, so that the dilution factor in such diluters varied little with particle size. The diluter was calibrated directly for each mean particle size at low h.d.a. concentrations under conditions of proportionality in the KUST apparatus, diluters having a dilution factor of around 10 being calibrated directly, while several diluters were connected in series for greater dilutions. The particle concentration in a developed diluted h.d.a. of droplet radius ~ 0.3 μm was determined by the classical ultramicroscopic method.

A large number of methods are theoretically available for determining particle size in h.d.a., but their applicability is greatly restricted in practice. Mention may be made of growing liquid h.d.a. particles in binary vapour mixtures[29,30], determining the size of sodium chloride particles by photometry of the flashes appearing on introduction of the particles into a hydrogen flame[31], and calculation of the radius from measurements of the capture coefficient for light ions[32].

Although a resolving power of the order of 5 Å has been achieved in modern electron microscopes, for several reasons no-one has yet been able to determine particle sizes less than 20–30 Å by this method, while for several substances the limit is considerably higher. In particular Megaw and Wiffen have found[33] that platinum and nickel particles of ~ 50 Å are either transparent to the electron beam or vaporise under its influence, and Young and Morrison[34] were unable to obtain micrographs of sodium chloride particles smaller than 200 Å.

Rich[35] suggested that, since the steady-state distribution of charges on aerosol particles in a bipolarly ionised atmosphere is given approximately by the Boltzmann formula and, as mentioned in the Introduction, h.d.a. particles are unable to carry more than one elementary charge, their size can be calculated from measurements of the percentage of charged particles. It must be borne in mind, however, that many hours are required for the charge on h.d.a. to reach a steady state under conditions of natural atmospheric ionisation, and therefore the aerosol must be subjected to extremely intense artificial ionisation—which is not usually done—for this method to be applied. Moreover, it is impossible by this method to obtain even a rough idea of the degree of polydispersity of the aerosol.

The well known method of determining the mobility of particles ("heavy" ions) in an electric field[36] permits the size distribution of only the charged particles to be measured. As the percentage of charged particles increases with increase in their size, this method will definitely overestimate particle size in the case of a polydisperse h.d.a.

Since the ability of particles to cause a vapour to condense depends not only on their size but also on their wettability, the presence of surface contamination, etc., the method of determining the particle size of h.d.a. from the critical degree of supersaturation of a vapour cannot give any reliable results[37].

An extremely simple and convenient method for determining the degree of dispersion of aerosols is based on measurement of the specific surface of a deposited aerosol from adsorption isotherms, but this method does not enable individual particles to be distinguished from aggregates, and it gives the mean size of primary particles and primary (i.e. coalesced or sintered) aggregates; on the other hand, in the case of h.d.a. which are highly concentrated by weight, in which a high degree of aggregation is unavoidable, only this method and electron microscopy are applicable in practice.

In several cases the Debye–Scherrer X-ray method, based on the broadening of the lines in the powder diagrams of very fine crystalline particles, proves to be extremely useful. It must only be remembered that the particles may consist of several crystallites, and results given by the Debye–Scherrer method relate to the dimensions of these latter. On the other hand, h.d.a. particles are quite often amorphous, and this can be established only by X-ray examination.

The most convenient way of measuring the particle size of h.d.a. is probably the diffusion method, based on passage of the h.d.a. through a circular or plane-parallel channel (or a "diffusion battery" comprising several channels) with measurement of the breakthrough (the ratio of the h.d.a. concentration at the outlet to that at the inlet to the channel). By means of the formulae deduced by Townsend and subsequently refined[38] the diffusion coefficient of the particles and hence their size can be calculated from the breakthrough value. Calculation shows that the charge on the h.d.a. particles has practically no effect on their breakthrough[39,40]. For a long time this method was employed only to determine mean particle size, but during recent years a series of attempts has been made to use it to determine the particle size distribution. The greatest theoretical interest is presented by Twomey's work[41], which showed that the distribution curve can be found from the curve of breakthrough against length of channel or rate of flow by means of the inverse Laplace transformation. Unfortunately, relatively small, unavoidable errors in the measurement of breakthrough lead to very large errors in the distribution function calculated in this way, and Twomey's method is probably applicable only to extremely polydisperse, e.g. atmospheric, aerosols. A method proposed by Pollak and Metnieks[42] enables the particles in an aerosol to be divided only into a small number of fractions.

The Laboratory for the Physics of Aerodisperse Systems uses a method based on the hypothesis that the particle size distribution in an aerosol is a logarithmic normal distribution[17,43]. This distribution is in fact observed more or less accurately in most aerosols, of both condensation and dispersion types. A computer has been used to calculate breakthrough curves through the channel as a function of the parameter $\mu = Dl/h^2\bar{u}$ (where $\bar{u}$ is the mean rate of flow in the channel, l its length, D the diffusion coefficient, and h the radius of a cylindrical channel or the half-width of a plane-parallel channel) for h.d.a. having different mean geometrical radii r_g and geometric standard deviation β_g. The breakthrough having been measured for a series of values of μ, the curve is selected which best fits the experimental points, and hence r_g and β_g are found. Then the Einstein–Millikan formula

$$D = kT[1 + A(\lambda/r) + (\lambda/r)\exp(-\gamma r/\lambda)]/6\pi\eta r \qquad (1)$$

(where η is the viscosity of the gas, λ is the mean free path of the gas molecules, and A, B, and γ are coefficients whose values are known for a series of substances) is used to calculate the size distribution curve for the particles regarded as spherical. For $r \leq 50$ Å, we can now use the simpler formula of gas kinetics

$$D = kTQ\lambda/6\pi r^2\eta \qquad (2)$$

in which we put $Q = 1.15$.

The apparatus used in the Laboratory for the Physics of Aerodisperse Systems to determine the particle size of h.d.a. by the diffusion method[17] is shown diagrammatically in Fig. 5. The aerosol leaves the producer A, is cooled to room temperature in the condenser B, and passes through the diluter D, where its concentration is brought to ~ 10^4 cm^{-3}. To obtain the desired rate of flow through the diffusion battery G (measured by means of the flowmeter F), part of the aerosol has been allowed to escape through E. After the battery the h.d.a. enters the KUST apparatus M and the nephelometer L. If the concentration of aerosol in the battery is to be diminished, part of it is passed through the filter K, and is mixed with the aerosol in such a way that the rate of flow in the KUST apparatus remains constant. To investigate h.d.a. having a mean particle radius of 25 Å, a set of diffusion batteries, differing in length and comprising eight cylindrical channels, is used. Over the mean particle radius range 25–100 Å, a set of sixty-channel batteries is used. For the investigation of aerosols of lower degree of dispersion, use can advantageously be made of measurement of deposition in plane-parallel slits.

With h.d.a. of particle radius ~ 10 Å, a difficulty is met when the diffusion method is used, in that all calculations for diffusion precipitation in channels start from the assumption that a parabolic flow profile has been formed in

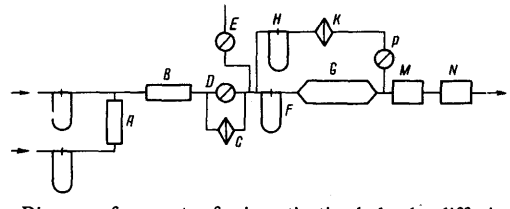


Figure 5. Diagram of apparatus for investigating h.d.a. by diffusion method.

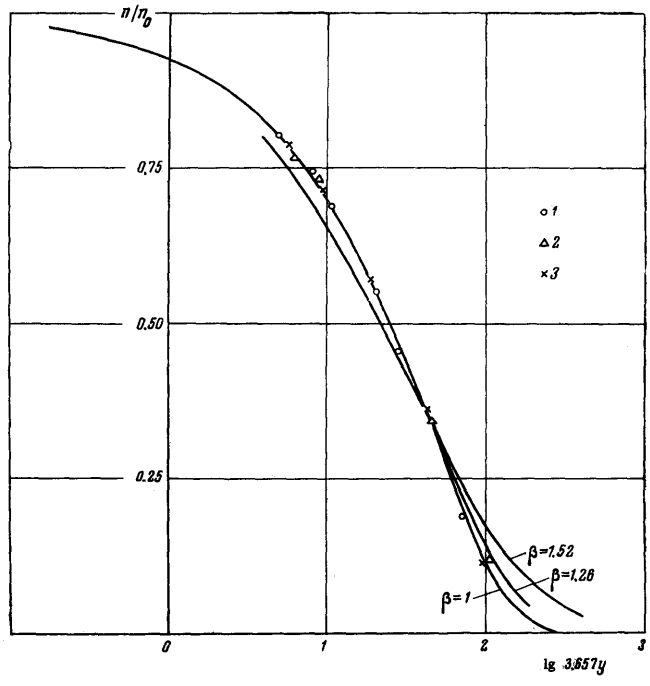


Figure 6. Theoretical curves and experimental values of breakthrough of sodium chloride aerosol through a battery of circular channels for different values of $\bar{r}$ (Å):
1) 11.8; *2*) 9.7; *3*) 7.0.

them. Naturally, the channels contain an entry section, deposition in which is significantly greater than calculated by the above method. It is very difficult to calculate theoretically the errors arising in this way, and the appropriate correction has been found experimentally.

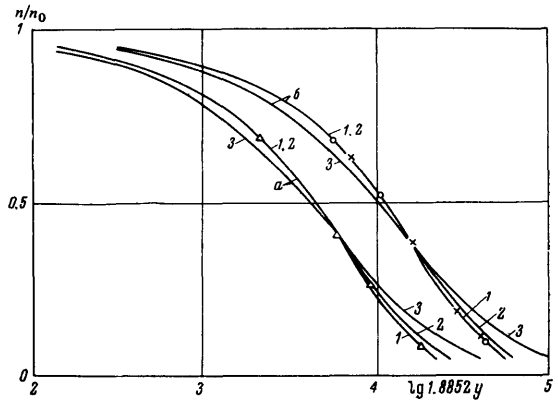


Figure 7. Diffusion breakthrough of dioctyl sebacate aerosols through an annular slit for different values of $\bar{r}$ (Å):
a) 100; *b*) 160; and of β_g: *1*) 1.0; *2*) 1.26; *3*) 1.54.

Fig. 6 illustrates the results of the measurements of particle size in sodium chloride h.d.a. mentioned in Section 2. The full lines have been calculated for different values of β_g (above the point of intersection the curves for $\beta_g = 1$ and 1.26 practically coincide). As is evident from Fig. 6, β_g is in any case less than 1.26 for the aerosols investigated. Fig. 7 shows analogous results for dioctyl sebacate h.d.a.[20] having a mean radius of 100 Å.

We thus see that the mean particle size of h.d.a. can be fairly accurately determined by the diffusion method, and the dispersion of sizes less accurately.

4. RATE OF COAGULATION OF HIGHLY DISPERSE AEROSOLS

As stated in the Introduction, the coagulation of h.d.a. takes place by a gas-kinetic mechanism: i.e. the coagulation constant K is given by the formula for the number of collisions between gas molecules. Nevertheless, a fairly substantial correction must be made to this formula for particles of radius 100 Å, i.e. for the upper limit which we adopted for the size of h.d.a. particles. No reliable experimental data on the magnitude of the coagulation constant of h.d.a. had been obtained until recently.

The chief difficulty in measuring the rate of coagulation of h.d.a. is the considerable loss of particles on the walls of the apparatus and connections due to the high diffusion coefficient of h.d.a. particles, which renders inapplicable the classical method, determination of the particle concentration in samples withdrawn from the chamber at intervals. Therefore a flow method was used in the Laboratory for the Physics of Aerodisperse Systems: an aerosol having a previously measured large counter concentration was passed with streamline motion through a vertical tube of capacity 2 litres.[28] Nephelometric measurements were made of the ratio of the concentrations entering and leaving the tube and of the mean residence time of the h.d.a. in the tube. In a separate experiment a greatly diluted non-coagulating h.d.a. was passed through the tube, and the correction for the diffusion losses of particles was determined.

The rate of flow varied from 10 to 17 litres min^{-1}, and the Reynolds number from 300 to 500. In order to diminish diffusion losses, the central portion of the flow (about half the total flow) was withdrawn isokinetically from the tube. It was established by special experiments that transverse mixing by convection did not occur in the cylindrical part of the tubes. Nevertheless, 6–14% of the particles, depending on the particle size and the rate of flow, were lost by diffusion in the tubes.

When the flow was made visible by means of an optically dense aerosol, appreciable circulation was observed in the diffusers, and most of the loss undoubtedly occurred in them. Since their volume was considerably less than that of the cylindrical portion of the tubes, it could be assumed that these losses preceded coagulation of the aerosols. The degree of coagulation (the ratio of the counted concentrations before and after coagulation) was therefore calculated by means of the formula $\epsilon = (n_1/n_2)/(n_1'/n_2')$, where n_1'/n_2' is the concentration ratio for the diluted (non-coagulating) aerosol, and n_1/n_2 the ratio for the undiluted (coagulating) aerosol.

To determine the residence time of the aerosol in the tube, which is practically identical with the coagulation time, pure air was first passed through the tube, and then after a certain time a coarse mist (or conversely), and the concentration of the mist emerging from the tube was determined as a function of time by means of a nephelometer. The mean residence time of the h.d.a. in the tube was calculated from the elution curves obtained.

These experiments gave mean values of K of 13.4×10^{-4} and 15.0×10^{-10} cm^3 s^{-1} for mean radii $\bar{r}$ of 25 and 45 Å respectively, the corresponding standard deviations being 11.5% and 12.5%. A detailed analysis of the sources of error in these measurements showed that the total square error in the value of K is 11.0%.

Comparison of experimental and theoretical values of K showed the latter to be considerably smaller (4.82 and 6.45×10^{-10} cm^3 s^{-1}). Such a large discrepancy is probably due to the effect of intermolecular forces on the coagulation constant. The "time lag effect" in intermolecular forces is known to diminish their magnitude at distances exceeding 200 Å so much that these forces play no appreciable part in the coagulation of coarse aerosols. With particles of radius 25 and 45 Å, on the other hand, the time lag effect can be neglected, and the potential for the intermolecular forces between two spherical particles can be calculated by means of Hamaker's[44] formula

$$V(\rho) = \frac{A}{6}\left[\frac{2r^2}{\rho^2} + \frac{2r^2}{\rho^2 - 4r^2} + \ln\left(1 - \frac{4r^2}{\rho^2}\right)\right] \qquad (3)$$

where ρ is the distance between the centres of the particles and $A = \pi q^2 \beta/6$, in which q is the number of molecules per unit volume of the substance and β is London's constant. The latter was determined for sodium chloride by Mayer from its ultraviolet absorption bands[45], and found to be $\beta = 1.8 \times 10^{-56}$ erg $Å^6$. The theory of collisions between gas molecules when forces of attraction operate between them shows that with this value of β the molecular forces increase the number of collisions, and hence the coagulation constant, by a factor of 2.19, independently of the particle size. From this we obtain theoretical values of 10.5 and 14.1×10^{-10} cm^3 s^{-1} for K, which show considerably

better agreement with the experimental results. The remaining discrepancy may be due to some polydispersity of the aerosols, which appreciably increases their rate of coagulation.

A coagulation constant of 13.4×10^{-10} cm^3 s^{-1} has been obtained[46] for dioctyl sebacate aerosols having $\bar{r} = 100$ Å. The gas-kinetic formula disregarding intermolecular forces gives $K = 10.5 \times 10^{-10}$ cm^3 s^{-1}, but this formula is not applicable in this case. A formula deduced by one of the present Reviewers[47], which is applicable at small Knudsen aerosol numbers exceeding unity, gives $K = 12.0 \times 10^{-10}$ cm^3 s^{-1} (without taking into account molecular forces).

It is curious that, for the coagulation of h.d.a., many authors use Smolukhovskii's formula even at the present time, substituting in it Eqn. (1) for the diffusion constant, and obtain excessively large values for the coagulation constant[48]. Without making due allowance for diffusion losses, some of these authors obtain the same excessively large experimental values for the coagulation constant.

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The systematic study of highly disperse aerosols began only quite recently, and it is still early to speak of their application to physics and technology, but we can already point to a number of problems in whose solution h.d.a. may prove useful. For the theory of the condensation of a vapour it would be extremely important to establish the relation between the critical supersaturation and the particle size of h.d.a., and for meteorology to determine the size of solution droplets formed in h.d.a. from hygroscopic substances at a given atmospheric humidity. By measuring the rate of vaporisation of h.d.a. particles (from the increase in their diffusion coefficient) of substances having a sufficiently low vapour pressure, we can determine the latter for particles which are so fine that the Kelvin equation cannot be applied. It may be hoped that refinement of the technique for measuring the coagulation constant of h.d.a. will yield a new method for evaluating intermolecular forces.

The finely divided powders obtained when h.d.a. settle out are also of great interest. In view of their immense specific surface and the structural disorder of the particles, they probably possess great chemical activity, and may find use as catalysts. Interesting data in the investigation of various physical phenomena depending on particle size—magnetic properties, the Mössbauer effect, etc.—can be obtained by the use of such powders. By measuring the heat of dissolution of finely divided powders of certain salts, it has been possible to determine their specific surface energy. It may prove possible to obtain high-quality diffusion membranes by sintering finely divided metal powders.

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