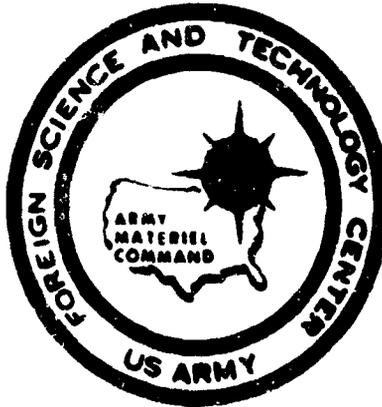


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HIGHLY DISPERSED AEROSOLS

By

N. A. Fuks and A. G. Sutugin

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13. ABSTRACT <p>In this review the authors examine the processes of formation of highly dispersed aerosols with particle dimensions less than 0.1 <math>\mu</math>, methods of generation and investigations of these aerosols and their physical properties, which differ radically from the properties of coarsely dispersed aerosols. Despite the tremendous importance of highly dispersed aerosols in meteorology and several other branches of science, despite the enormously important role that they play in the processes of formation of condensation aerosols in nature and in science, there is practically no review-monographic literature on this subject and the review which we bring to the attention of the readers is an attempt to bridge this gap.</p>			

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## 51. Introduction. The Basic Properties of HDA

In this review highly dispersed aerosols (HDA) are defined as aerodispersed systems with particulate dimension<sup>1</sup>  $< 1,000 \text{ \AA}$ . In air at atmospheric pressure this corresponds to a Knudsen number  $Kn$  (ratio of mean free path of gas molecules to particle radius) greater than unity. The most important property of HDA with Knudsen number  $Kn \gg 1$  is that the processes of pulse, energy and mass transfer from the particles to the medium and back is described in this case by the gas kinetics formulas, i.e., the particles can be regarded simply as gigantic gas molecules. Therefore, the resistance of the medium to the motion of the particles, the rate of evaporation (mass reduction) and the rate of heat transfer to them, as well as the rate of thermophoresis are proportional to the square of the radius of the particles. The "Knudsen aerosol number", i.e., the ratio of the apparent mean free path of the particles themselves to their radius, when  $Kn \gg 1$ , is also greater than unity and therefore the rate of coagulation of HDA is expressed by the formula for the number of collisions between gas molecules, and the coagulation constant increases with particle dimension.

For HDA with a Knudsen number greatly exceeding unity it is necessary to add to the above-mentioned formulas correction factors that increase as  $Kn$  diminishes. For small  $Kn$ , however, i.e., in coarsely dispersed aerosols, all above-mentioned processes are subordinate to completely different laws, which are derived from the equations of hydrodynamics, thermal conductance and diffusion in continua.

The vapor pressure of HDA particles greatly exceeds the equilibrium pressure above a flat surface of the materials of the particles.

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<sup>1</sup> In this article the dimension is always particle diameter ( $d$ ).

Diffusion of light by HDA obeys the Rayleigh equation, and the intensity of the diffused light is so small that the analysis of HDA by macro-optical methods is fruitless; under ordinary conditions of illumination and observation HDA particles are invisible under the ultramicroscope.

Brownian motion of HDA particles is so vigorous and their inertia and sedimentation rate under the influence of gravity so small that the setting of HDA on walls, obstacles, etc. takes place exclusively as a result of diffusion. The charges taken on by particles with radius  $\leq 0.03$  micron in a bipolar ionized atmosphere do not exceed one elemental charge, and the fraction of the charged particles decreases with diminishing dimension.

In every sense mentioned herein HDA sharply differs from aerosols with the dimension  $> 1,000 \text{ \AA}$ , which up to now have been the basic target of aerosol investigations.

We mention also that with consideration of the above statement concerning the charges of HDA particles their electrical mobility exceeds  $10^{-4} \text{ cm}^2/\text{v}\cdot\text{sec}$ ; thus the charged part of atmospheric HDA belongs, in the terminology of aerophysicists, to "medium" and "heavy" atmospheric ions.

## CHAPTER 1

### FORMATION OF HDA AND PRODUCTION METHODS

#### §2. Formation of Condensation HDA

The investigation of the theory of the formation of HDA should begin with the following question: In exactly what cases during the condensation of vapor are extremely fine particles formed? The average mass of the particles is equal to the ratio of the mass of the condensing vapor to the number of particles formed. It follows from any theory of spontaneous condensation that the rate of nucleation (i.e., formation of seeds of the new phase) increases more rapidly than the first order of supersaturation, whereas the rate of condensation growth of particles increases approximately in proportion to supersaturation. Therefore, the average particle dimension in the forming aerosol in the absence of coagulation should be less, the greater supersaturation is, i.e., the greater the extent of supercooling of the vapor (in the case of instantaneous temperature drop). In actual conditions cooling takes place at a certain finite rate and the formation of the aerosol, including nucleation and condensation growth of the seeds, takes place during the entire cooling period. The faster the vapor cools at the given initial and final temperatures the smaller the amount of vapor that is used up in the growth of particles formed in the early cooling stage at a comparatively low supersaturation and the larger the number of particles formed.

As regards the influence of the nature of the substance on the dimension of the aerosol particles, most important here is the slope of the curves of the vapor pressure temperature dependence. Given the same cooling conditions of the vapor, substances with steeper curves produce more highly dispersed aerosols. This steepness for a given substance increases as temperature decreases. Therefore, if the vapor of a substance that is saturated at temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ ) is instantaneously cooled by  $\Delta T$  degrees, a more highly supersaturated and more highly dispersed aerosol is formed in the second case. Here both high supersaturation and a reduction in the equilibrium concentration of the vapor in the forming aerosol are important. Meanwhile, if this concentration is not very low the HDA is extremely unstable: within the HDA the process known as "devouring" of the smaller particles by the larger takes place at a rapid rate. This process is attributed both to isothermic fractionation of the vapor from fine particles to large and to the effect of local temperature fluctuations in the aerosol: even with an extremely small temperature rise the finer particles evaporate completely, and with subsequent cooling the liberated vapors condensed on individual larger particles. Therefore, the HDA can be made from substances that are volatile at room temperature, for instance, water, by simply a rapid cooling of the vapor to the temperature of liquid nitrogen.

Ordinarily the formation of HDA takes place through spontaneous condensation, since the concentration of foreign condensation nuclei, including gas ions, is small in comparison with the concentration of the nuclei that form spontaneously at high supersaturations. During the formation of HDA in plasma burners, on the other hand, during condensation of cesium vapors in a coronal discharge in flow from a Laval's nozzle, etc., i.e., at extremely high ionic concentrations, condensation apparently takes place on the gas ions.

We excluded from the above examination the coagulation of particles which can be accompanied by coalescence or sticking together. Meanwhile, as will be pointed out below, coagulation plays a fundamental role in the formation of HDA at moderate concentrations of the vapor.

Classical nucleation theory [1] is thoroughly discussed in the literature. Therefore, we will simply discuss the basic premises of the theory. It is assumed that a supersaturated vapor represents a mixture of single molecules and molecular aggregates, the concentration of which, according to general theory of thermodynamic fluctuations, is an exponential function of their free enthalpy of formation  $\Delta G$ . The dependence of  $\Delta G$  on the number of molecules in aggregate  $g$  in a supersaturated vapor has the maximum. Each aggregate may, with a certain probability, get larger as the result of the sticking to it of colliding molecules or may shrink through evaporation. For aggregates with dimensions exceeding the critical value  $g^*$  the corresponding maximum  $\Delta G$ , the probability of growth is much greater than the probability of evaporation. Such "super critical" aggregates are viewed as nuclei of the new phase. The change with time of the concentration of the aggregate containing  $g$  molecules is expressed through the equation

$$\frac{dN_g}{dt} = \alpha_g N_{g-1} - \alpha_g N_g + \beta_g N_{g+1} - \beta_g N_g \quad (2.1)$$

where  $\alpha_g$  is the probability of collision of the aggregate with a vapor molecule,  $\beta_g$  is the probability of evaporation of molecules from the aggregate. The value of  $\beta_g$  in classical theory is expressed through  $\alpha_{g-1}$  using the principle of minute equilibrium. When  $g^*$  is sufficiently large the set of equations of the form (2.1) for  $g$  from 1 to  $g^*$  can be replaced by the differential equation

$$-\frac{dN_g}{dt} = \frac{d}{dg} \left\{ \alpha_g \frac{dN_g}{dg} + \beta_g \frac{dN_g}{dg} - \beta_g N_g \right\} \quad (2.2)$$

which is essentially the equation of the "diffusion" of aggregates along discontinuous axis  $g$ . Under stationary conditions nucleation rate  $I$  can

be found in the assumption that supercritical particles are eliminated from the system and are replaced by a quantity of vapor equal in mass through the equilibrium equation to

$$-1 - \sum_k z_k \frac{\partial \Delta G(g)}{\partial g} = \sum_k \frac{\Delta G(g)}{RT} \frac{\partial \Delta G(g)}{\partial g}, \quad (2.3)$$

During the formation of HDA, because of the high values of supersaturation required for this purpose,  $g^*$  usually does not exceed 10. Therefore, the method used in classical theory of expressing the free enthalpy of nuclei, in which they are viewed as droplets of a liquid having the macroscopic properties of the latter, is obviously unsuitable. Moreover, when  $g^*$  is small the discreteness of the  $g$  axis increases and it cannot be regarded as continuous. Very often the process leads to supersaturation, i.e., cooling of the vapor or vapor-gas mixture, takes place simultaneously with the formation of nuclei of the new phase and with the growth of the particles formed. Under such conditions the temperature, concentration of the vapor and supersaturation change constantly throughout the process, and this makes it impossible to solve equations of the form (2.2).

There is, in addition to the classical method, another approach to the problem of nucleation, known as the "theory of constant nucleus dimension" ("constant-number theory"). The value of  $g^*$  in this series is seen to be small, slightly larger than 2, and practically independent of nucleation conditions. The probability of evaporation of a nucleus containing  $g^* + 1$  molecules is ignored and the concentrations of the subcritical aggregates are considered equal to the equilibrium concentrations. In classical theory, however, the difference between stationary and equilibrium concentrations of small aggregates is also small. The intuitive considerations that make up the foundation of the theory of constant nucleus dimension were first advanced by LaMer [2] and Courtney [3]. Based on similar considerations, Christiansen [4] attempted to evaluate the time required for reaching equilibrium concentrations of subcritical aggregates after the establishment of supersaturation in a monomolecular vapor by solving a system of four equations of the form (2.1). These estimates, however, were only of a qualitative character because of the lack of definition of the free enthalpy of formation of small aggregates.

A method for calculating this value was advanced by Reed [5] who expressed the chemical potentials of aggregates of the molecules of inert gases through sums with respect to the states of these aggregates. For this purpose, Reed assumed that aggregates of each dimension exist only

in the most stable three-dimensional configuration, that within them exists only a paired relationship between the nearest neighbors, described by the Leonard-Johns equation, and that the molecules making up the aggregate retain their rotational degrees of freedom. Reed calculated the chemical potentials of aggregates of nitrogen molecules with  $g \leq 8$ . Calculation of larger aggregates is complicated by a larger volume of calculations and greater error related to lack of consideration of various three-dimensional configurations of the aggregates. The latter error can be eliminated by using, instead of Reed's method, methods of calculating reduced group integrals, although even the latter methods for such calculations require a much larger volume of calculations than Reed's method. Sutugin and Fuks [6] advance a method of calculating nucleation of high supersaturations, based on the combining of the theory of constant nucleus dimension with Reed's calculations. According to this method the process is broken down into several tens or hundreds of time intervals  $\Delta t$ . It is assumed that at the beginning of each interval the concentration of subcritical aggregates corresponds to values that are equilibrium values for temperature and concentration of the vapor which exists at that particular moment. The number of nuclei of dimension  $g^* + 1$  formed during time  $\Delta t$  is determined with the aid of an equation of the form (2.1), but without consideration of the terms, described decomposition of these supercritical nuclei. The expenditure of vapor to the growth of particles formed in the preceding intervals  $\Delta t$  is considered simultaneously. This method can also be used for nucleation of associated vapors. In this case it is also necessary to consider the probability of collisions of associates with each other (if such collisions lead to the formation of supercritical nuclei) and with supercritical particles.

This method was used for calculating the condensation of silver vapors in a hot turbulent stream of argon flowing into cold stagnant air in the range of silver concentrations from  $5 \cdot 10^{14}$  to  $5 \cdot 10^{16}$  atoms/cm<sup>3</sup> (weight concentration 0.5-50 g/cm<sup>3</sup>). During the calculation it was found convenient to use the value of the integrals equal to the average interval between consecutive collisions between a critical aggregate and vapor molecules. This simplified calculation, since it could be assumed that during time  $\Delta t$  all aggregates of dimension  $g^*$  pass into the supercritical range of dimensions. It was understood that the value of  $\Delta t$  was not constant during the calculation, but increased as the vapor was used up. Since  $\Delta t$  is quite small ( $10^{-5}$  to  $10^{-7}$  sec), the equilibrium concentrations changed not more than by two during transition from one interval to another, and on the other hand, the value of  $\Delta t$  was large enough so that the concentration of aggregates took on a new value, corresponding to the beginning of a new interval. Therefore, it could be assumed that in each interval the concentration of critical aggregates was equal to the equilibrium concentration, determined from the conditions that existed at the beginning of the interval. The dimension of the critical nuclei

under the above-stated conditions was 2 to 6 atoms, depending on temperature and concentration, so that the term "theory of constant nucleus dimension" should be regarded as incorrect. The concentration of particles formed was quite high-- $10^{13}$  to  $10^{14}$  cm. Therefore, coagulation took place in parallel with the nucleation and condensation growth of the particles. The coagulation of very fine particles may be accompanied by their sticking together or coalescence, even at relatively low temperatures and leads to the formation not of aggregates, but of continuous particles. With sufficient smallness of intervals  $\Delta t$  the changes caused in any such interval by any of three simultaneous processes--nucleation, condensation growth and coagulation, are relatively minor and it can be assumed that these processes take place independently, preceding each other in time and each interval.

In the literature are described several programs [7-11] for calculating the coagulation of polydispersed aerosols, based on the solution of a system of linear differential equations of the form

$$\frac{df(g)}{dt} = - \sum_{i=1}^{\infty} K_{ig} f_g f_i + \sum_{j+k=g} K_{jk} f_j f_k \quad (2.4)$$

Present-day computers make it possible to solve a system containing not more than several hundred such equations. Therefore, these methods are suitable only for the calculation of processes in which the particles formed contain not more than 100 to 150 primary particles. During the formation of HDA, primary particles are single molecules and the smallest value of [illegible] at which the calculation should be started is 1. For  $g$  the smallest value is  $g^* + 1$ ; for  $g \leq g^*$  the concentrations are assumed to be equilibrium at each given moment. Since, as a result of the process, particles measuring  $100 \text{ \AA}$  may form, i.e., consisting of  $10^5$  and more molecules, the above-mentioned programs are not suitable for the calculation of the formation of aerosols that are not very highly dispersed. Rosinski and Snow [12] advanced a simplified program based on the assumption that all particles consist of  $2^i$  molecules, where  $i$  is a whole number. The collision of two particles of the class  $2^i$  leads to the formation of particles of the class  $2^{i+1}$ . Further, it is assumed conditionally that during collisions of particles of classes  $2^i$  and  $2^{i+1}$  particles of the class  $2^{i+1}$  are also formed, but in the quantity  $(2^i + 2^{i-1})/2^{i+1} = 0.75$  of the number of particles of class  $2^i$  that participated in the collisions. In collisions, however, particles of classes  $2^i$

and  $2^{i-j}$ ,  $j > 1$ , the dimension of the former decreases, but their number increases by a factor of  $(2^i + 2^{i-j})/2^i$ . Of these assumptions, the former leads to an overstatement of the rate of mass transfer along the axis of particle dimension, and the latter to an understatement; the errors attributed to these assumptions are at least partially compensated.

This program was combined with the above-described method of calculating nucleation and condensation growth [6]. Both the calculation and experimental results obtained by electron microscopic analysis of particles sampled at various stages of the formation of aerosols. The determination of the capacity of the powders formed by the precipitation of these aerosols for coalescence prompted the conclusion that the process by which the HDA of silver is formed in this range of concentrations of the vapor can be broken down into six stages. 1. Nucleation and condensation growth. 2. Nucleation, condensation growth and coagulation, accompanied by the agglutination of particles. 3. Coagulation with agglutination and condensation growth. 4. Coagulation with agglutination. 5. Coagulation, accompanied by agglutination of fine particles and coalescence of large. 6. Coagulation, leading to the formation of aggregates of particles held only by cohesion forces. The dispersion of the aerosols obtained in this work, determined by measurement of the specific area of the sediments, was governed almost exclusively by coagulation, accompanied by agglutination of the particles. Therefore, the average particle dimension was proportional to the cube root of the vapor concentration.

At very large supersaturations of the vapor the labile state may be reached, i.e., the thermodynamic barrier between the phases may vanish, and in this case the formation of aggregate, even from two molecules, becomes an irreversible process. The assumption of the reaching of the labile state was made arbitrarily by Rozinski and Snow [12] for calculation of the condensation of  $\text{Fe}_2\text{O}_3$  vapors and by Stockham [13] for silver vapors.

By calculating the condensation of Ag vapors under conditions similar to Stockham's experimental conditions, Sutugin and Fuks found that the labile state in this case is not achieved. However, since in the final analysis the dispersion is determined by coagulation, accompanied by particle agglutination, in view of the asymptotic character of coagulation the path of condensation in the early stages of the formation of the aerosol has little effect on the final result. This governs the applicability of the Rozinski-Snow method to those cases where the labile state is not reached, and explains the fact that Stockham obtained reasonable results.

In the case where  $g^* = 2$  the rate of nucleation is determined by the ratio between the rates of formation of trimer and dissociation of the dimer. The formation of the bonded state during collision of two molecules

was examined [16], although the lifetime of the vapor aggregate formed as a function of the temperature, reaction potential and geometric parameters of collision, could be found only by numerical methods. Therefore, the results [16] for the calculations of the process of aerosol formation are still inapplicable. It should be pointed out that the concentration of dimers in nitrogen, calculated by this method, differ somewhat from the concentration calculated by Reed's method [6].

In those cases where  $g^*$  is quite large and supersaturation changes little during the relaxation time of the nucleation process, as determined by the solutions of time-dependent diffusion equation (2.2), it is possible to use the ordinary stage by stage calculation method, in which the nucleation rate in each stage is determined by stationary solutions of classical theory. This method, of course, is not applicable in the presence of coagulation, nor for description of the condensation of associated vapors. Using this method Griffin and Sherman [15] demonstrated that HDA can form as a result of condensation of copper vapors that flow through a Laval's nozzle at high mach numbers. Such a description of consecutive calculations of condensation in the nozzles using stationary solutions of classical theory can be found in the literature [16, 17].

Under the condition of slow change in supersaturation the condensation process can be described with the aid of differential equations that express changes in time of temperature, vapor concentration and nucleation rate, and also of the equations of continuity and adiabatic expansion in the case of condensation in nozzles. The solution of such an equation system for the simplest cases and the large number of assumptions can be found analytically, i.e., the theoretical dependence of the number of particles formed and their mass on time can be found. Solutions of this type were found by several authors [18-20]. The attempt of Buykov and Bakhanov [21] to avoid simplification assumptions required the use of numerical solution methods with the aid of computers.

Very often the formation of condensation HDA is related to chemical reactions in the gas phase, for instance during the production of soot by the pyrolysis of hydrocarbons, production of metals by decomposition of chlorides and carbonyls, etc. Three cases of the formation of condensation aerosols as a result of chemical processes can be singled out. The first case is where the chemical reaction leads to the formation of condensed vapor and takes place so rapidly that it is finished before nucleation can begin. In this case the calculation of the condensation process is the same as that of "physical" condensation. In the second case the reaction takes place in parallel with condensation, but the aerosol particles formed have no effect on the reaction. In this case the chemical reaction can be taken into account by the consecutive

calculation of condensation. For this purpose it is necessary to consider not only the expenditure of vapor for growth and formation of the particles, but also the formation of new portions of vapor as a result of the chemical reaction, and also, if necessary, the thermal effect of the reaction. A calculation program of this type was described by Dunhem [22], who was able in this way to establish the relationship between the rate of formation of  $H_2SO_4$  and the rate of nucleation in these vapors. The third case is where the reaction can be catalyzed on the surface of the forming particles. This case poses the greatest difficulties in calculation and so far no mathematical model has been devised for such a process. Nevertheless, it should be pointed out that Tesner [23] proposed a method permitting calculation of the dependence of the number of soot particles formed by pyrolysis on time if the distribution of the particles with respect to dimensions in the final aerosol is known.

### §3. Production of HDA by Physical Condensation of Vapor

The methods of producing condensation HDA can be classified on the basis of the method of achieving supersaturation of the vapor: during "physical condensation" supersaturation is achieved by cooling the vapor or gas-vapor mixture, during "chemical" condensation, a substance possessing extremely low vapor tension at the reaction temperature is formed as the result of the gas reaction. The vapor can be cooled by mixing it with a cold gas, by heat exchange with a cold body (walls of refrigerator, coolant, etc.), by adiabatic expansion, or by a combination of these methods.

The simplest method of HDA generation by mixing, but hardest to control, is heating of high-boiling solids or liquids in a turbulent flow of cold gas. Mixing of the vapor of the heated material and the gas and the initial nucleation stage take place here near the surface of the material. In the absence of flow or in laminar flow of the gas mixing takes place very slowly and, in accordance with what was said in §2, coarsely dispersed aerosols are generally formed. In this method the presence of more volatile contaminants which also form HDA on heating pose serious difficulties, although in most cases these aerosols can be distinguished from the basic aerosol on the basis of the criterion that their concentration gradually diminishes by measure of evaporation of the contaminants [24]. When the concentration of the aerosol remains constant over a long period of time it can be assumed that it consists of the basic material. The method is often formulated in such a way that the vaporized substance is applied as a thin film on a high-melting wire heated by an electric current. This is the way that HDA is obtained from various salts. A serious deficiency of this method is the fact that in time the concentration of the aerosol formed and the particle dimension continually decrease.

In the case of NaCl at a temperature of 450°C the particle dimension diminishes for 5 to 7 hours, reaching values of 100 to 300 Å [25]. This is attributed to the gradual recrystallization of the salt on heating, leading to a reduction in its rate of evaporation. To obtain time constant aerosols it is possible to resort to the aging of the NaCl layer for several hours and replacing it after one day of work. The HDA thus obtained is very polydispersed.

HDA can also be generated by the calcination in air of pure metallic wires; first purpose Pt and W are most often used. The concentration of the HDA formed is quite constant in time and is more or less satisfactorily reproducible, thanks to which these types of HDA are often used as condensation seeds and for the production of monodispersed aerosols. The mechanism of the formation of HDA from the above-mentioned metals consist, apparently, in their surface oxidation and evaporation of oxides that are considerably more volatile than the metals themselves. This is evidenced by the fact that the formation of oxide HDA begins at temperatures at which the vapor pressure of the metals is infinitesimally small: from platinum at 200 [28] or 255°C [27]; from tungsten at 300 or 500°C [28]; from nickel at 650°C [27] and 950°C [24]. Such great differences in the determination of the temperature at which HDA begins to form are attributed to the difficulty in detecting aerosol particles of nearly atomic size and to the presence of hard to remove contaminants in the metals. These aerosols are also extremely polydispersed [27-29]. During the blowing of a platinum wire heated to 300°C with a stream of air at the rate of 1 liter per minute the concentration of aerosol reached  $\sim 2 \cdot 10^5 \text{ cm}^3$  and the average particle dimension was about 40 Å [28]. A  $\text{CrO}_3$  aerosol with a particle dimension of  $\sim 15 \text{ Å}$  [29] was obtained from a Nichrome wire heated to 1,000°C.

The analogous method is sublimation of a substance in a rarefied gas: the substance, placed in a vessel with a rarefied inert gas is calcined either with a tungsten coil [30-32] or by the induction method [33, 34]. This method was first posed by Gen, Ziskin and Petrov [30] for the production of aerosols of aluminum, and then was applied to a large number of other metals. The dimension of the particles generated by this method diminishes with a reduction in the rate of evaporation of the metal and pressure of the gas, where the minimum average dimensions of the particles obtained by this method is  $\sim 200 \text{ Å}$ . More highly dispersed aerosols could not be obtained, since at low vapor concentrations the dimension of the particles is practically independent of the gas pressure and concentration of the vapor. Turkevich [34] analyzed at length the mechanism of the formation of aerosols by this method. By placing the apparatus for the sampling of aerosol particles at various distances from the vapor source he was able with the help of electron microscopy to trace the process of the formation of aerosol or, at least, the last stages of its formation and arrive at the conclusion that the aerosol

is formed in three stages, corresponding to the first, third and fifth stages on p. 12 of this review. A reduction in the dimension of the particles as the pressure of the inert gas is increased, is in Turkevich's opinion, the result of acceleration of vapor diffusion and the resultant increase in the rate of its cooling.

In [13] is described a flow version of this method: silver vapor from a crucible heated by the induction method is mixed with rarefied argon flowing past the crucible. In this way it is possible to produce silver aerosols with an average particle dimension  $\approx 40 \text{ \AA}$ . The particle dimension increases as the vapor concentration is increased, but is practically independent of the argon pressure. Probably, the mixing of vapor in this case with the cold gas takes place basically as the result of turbulence.

The production of aerosols in rarefied gases is in itself, of course, extremely useful in the analysis of the properties of aerosols at reduced pressure, since the problem of a substantial change in pressure in an aerosol without the loss of particles, their coagulation, etc. is extremely complex. For this very reason, however, this method is not suitable for investigation of aerosols under normal conditions.

More improved HDA generators, in which comparatively large quantities of the substance are heated in a thermostat furnace in a slow gas flow, are now in use. Here the gas is practically saturated with the vapor and is then rapidly mixed with cold gas. Under these conditions the concentration of the vapor remains constant in time, which facilitates constancy of concentration and dispersion of the aerosol formed. Two versions of such generators are now in use. In one version, mixing is accomplished in a free gas volume, for instance, with the outflowing of a hot turbulent stream of vapor or vapor-gas mixture into a large volume of cold gas. In this case all the vapor is condensed in the volume. In the second version mixing takes place in a T-type diffuser nozzle, etc., and most of the vapor by far is condensed on the mixer walls.

A generator of the first of these two types was used in the above-mentioned work [6]. The dependence of the dispersion of the HDA on the operating mode of such a generator was investigated by way of example of an aerosol obtained through the condensation of  $\text{MoO}_3$  vapor in a hot air stream flowing into cold air at the rate of 8 to 580 m/sec [35]. In the range of vapor concentrations in the stream from 0.1 to  $100 \text{ g/cm}^3$  it was possible to obtain aerosols with an average particle dimension 70 to  $1,000 \text{ \AA}$ . The particle dimension decreases to some limit as the vapor concentration is decreased and the linear flow rate is increased, and at some constant linear flow rate, as the nozzle diameter is reduced. It

is interesting to note that the dispersion of aerosols formed during condensation in a stream at the very same vapor concentrations was higher than in a heat exchange generator (see below). The influence of flow rate and nozzle diameter was explained with the aid of the equation presented in work [6] for mixing rate in a submerged stream, showing that this rate increases with the indicated change in the above-mentioned parameters. In the range of low concentrations ( $< 1 \text{ g/m}^3$ ) the increase in particle dimension as the way concentration is increased is not very noticeable, but intensifies as concentration is increased. This can be explained by the increasing influence of coagulation, accompanied by coalescence of the particles.

The formation of HDA in arc or plasma burners takes place in much the same way. The substance is added either to the material of the electrodes or in the form of a powder to the gas stream. The stream of incandescent gases is cooled as a result of mixing with cold gas or with atomized coolant. Condensation of the vapors on cooling takes place apparently on ions. According to the given electron microscopic analyses [34, 36-37], particle dimension in the aerosols thus obtained is 25 to 1,000 Å, and the average dimension, in terms of mass, may vary from 200 to 800 Å. By vaporizing metals in an atmosphere of inert gases and in a reducing atmosphere it is possible to produce metal aerosols, and in an oxidizing atmosphere, oxide aerosols. It is interesting to note that particles of aerosols generated with the aid of arc or plasma burners are usually amorphous. Holmgren, Gibson and Sheer [37] showed that the dispersion of aerosols can be increased by using induced cooling of the gases flowing from the arc. Selover [38] investigated the formation of nickel aerosol during cooling of argon plasma containing nickel vapor. To argon, fed into a plasma burner, atomized nickel carbonyl was added. Since the decomposition of carbonyl took place at a very high temperature it can be assumed that it preceded physical condensation. In the range of carbonyl concentrations between 0.006 and 0.025 g/ the particle dimension of the aerosol obtained varied within the limits of 15 to 150 Å. For the purpose of rapid cooling the argon stream was sprayed with a coarsely dispersed aerosol of cooled isopropyl alcohol. With an average particle diameter (determined by BET (Brunauer, Emmett and Teller) method), of 200 Å practically all particles were included in the dimensional range of 30 to 300 Å. Safronov [39] showed that it is possible to produce a highly dispersed soot aerosol by condensing carbon vapors formed by the decomposition of benzene in plasma.

By the plasma method it is possible to put even high-blowing substances (with the exception of thermally unstable materials) into the aerosol state, and in large quantities at that. Unfortunately, the mechanism of processes that take place during condensation in cooled plasma jets has not yet been sufficiently investigated.

Let us turn now to generators in which vapor and gas are mixed in narrow mixers. A mixer generator is described [40] that is designed for the production of highly dispersed aerosols from salts, for instance, from NaCl, consisting of a quartz tube placed in an electric furnace, with one side fitted with a T-pipe with an inside diameter of 8 mm. In the tube are placed ceramic rings, coated with a volatile substance, and through it is passed air at the rate of 0.1 to 0.5 l/min. In the T-pipe this flow is mixed with a large volume of cold air (5 to 20 l/min). To prevent condensation of the vapors on the walls prior to mixing a heater is installed in the generator. This generator is capable of producing rather monodispersed NaCl aerosols with an average particle dimension of 14 to 100 Å. The maximum calculated concentration of the particles which can be achieved increases with dimension and varies between  $10^3$ -- $10^9$ /cm<sup>3</sup>. By changing flow parameters--flow rate of air through the furnace and through the T-pipe, current strength in the furnace windings and heater, it is possible to change the average dimension and concentration of the aerosol particles in the above-mentioned limits. The generator is very stable in operation and produces satisfactorily reproducible results. A generator of this type was used successfully [41] for the production of radioactive NaCl HDA.

The production of reproducible monodispersed aerosols of dioctyl sebacinate with an average particle radius of 30 to 300 Å is described [42]. These aerosols were obtained in a mixer generator of the type KUST, described in §6, and NaCl with an average particle dimension of 34 Å was used as the seeds. The particle dimension of the dioctyl sebacinate could easily be changed by varying its vaporization temperature, concentration of condensation nuclei and ratio of the flow rates of the gas-vapor mixture and cold air.

Cooling of the vapor-gas mixture was possible also by heat exchange with the walls of the apparatus. Precisely the same method was used in the well-known Sinkler-LaMer monodispersed aerosol generator. LaMer [43] showed that it is possible to use this generator for the production of sulphuric acid HDA. According to his report it is thus possible to generate the HDA with a particle diameter of 20 Å.

Matiyevich and Kerker et al., [44-46] modified the LaMer generator and used it for the production of aerosols of various mineral salts, such as AgCl, NaF, NaCl; these authors analyzed in detail the influence of the gas flow rate in the generator and the evaporator temperature of the dispersion of the aerosol formed under conditions of spontaneous condensation and discovered that the average particle dimension increases as these parameters are increased. The reason for the increase of the particle dimension with increasing flow rate is not completely clear; unfortunately no detailed plan of the modified generator has yet been published. In these works the authors managed to produce particles measuring between 10 and 1,000 Å. The degree of polydispersion of the aerosols depended little on the average particle dimension and the standard geometric deviation was 1.15 to 1.2.

In a number of works heat exchanger generators were used for the production of NaCl HDA with high weight concentrations (up to  $1 \text{ g/cm}^3$ ) for the purpose of further precipitation of these aerosols and production of highly dispersed powders [47-49]. An increase in the particle dimension with increasing vapor concentration was also noticed in these works. Due to heat exchange it was impossible to achieve very high cooling rates, and consequently high vapor supersaturations. Therefore it is difficult to produce aerosols with particle dimensions less than  $100 \text{ \AA}$  in heat exchanger generators. The formation of  $\text{MoO}_3$  aerosols by passing hot air containing vapors of this substance at a rate of 1 to 28  $\text{l/min}$  through a quartz water cooler with a diameter of 20 mm was investigated in [35]. At greater concentrations of  $0.002\text{--}8 \text{ g/m}^3$  the average dimension of the particles obtained, determined from a certain BET method for specific area of powders obtained by the precipitation of these aerosols, was  $130\text{--}1,000 \text{ \AA}$ . The investigators were not able to observe whether or not the flow rate has any clear influence on the dispersion of the aerosols.

In addition to heat exchange and mixing with cold gas, adiabatic expansion may also be used as a method of cooling. The condensation of the vapor during adiabatic cooling takes place in the nozzles of supersonic wind tunnels, where it is an undesirable phenomenon, the elimination of which requires implementation of special measures (air drying, heating of nozzle walls, etc.). On the other hand, the formation of HDA, particularly of strongly contaminated HDA, in nozzles is of considerable interest for the creation of electric colloidal motors.

For all substances except helium, a drop in the equilibrium pressure of the vapor, attributed to a reduction in the temperature during adiabatic expansion, takes place more rapidly than a drop in static pressure. Therefore sufficiently strong isoentropic expansion of the vapor-gas mixture or even of the pure gas, may lead to the creation of high supersaturations. The growth rate of supersaturation can be extremely high, therefore the formation of HDA even from such volatile material as water is observed in wind tunnels. The lifetime of these aerosols, however, is quite short, since particles evaporate at high temperatures in the shock wave. The dimension of ice crystals formed in a laval nozzle at mach 5 was estimated [50-51] on the basis of their inertial properties and rate of evaporation in the shock wave. Particle dimension was about  $14 \text{ \AA}$ , and they were about identical in magnitude, independent of the concentration of water vapor. Condensation in Laval nozzles was examined [57, 53] from the point of view of the possibility of producing a ray of charged particles suitable for use in an electroreactive motor.  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgCl}_2$  and  $\text{AlCl}_3$  vapors were passed through a heated nozzle in a vacuum [57]. For analysis the particles were precipitated on a screen placed in the nozzle. In this manner it was possible to obtain particles with an average dimension of 100 to  $1,000 \text{ \AA}$ . Cadmium vapors flowing through a nozzle were condensed in the field of a positive coronal discharge [55], whereupon particles measuring  $\sim 100 \text{ \AA}$  were obtained.

Cooling of the vapor-gas mixture due to both adiabatic expansion and mixing with cold gas and ray emission apparently takes place during the production of aerosols by the flashing wires method [54-56]. In this method a high voltage discharge of considerable power (about 1 kg per milligram of wire) is fed to a thin wire fastened between massive electrodes. The wire is converted instantly into a plasma "cable", on cooling of which an aerosol is formed. In an atmosphere of inert gases of all metals, and in air, metal aerosols are formed only from the noble metals. In the presence of nitrogen and oxygen nitrides and oxides are formed. The size of the particles usually falls between 50 and 1,000 Å. The average particle dimension depends upon the material from which the wire is made and diminishes as the power of the discharge is increased. The fact that during instantaneous dilution of the aerosol cloud it is possible to produce aerosol consisting of individual non-aggregated spheres [54] indicates that condensation growth, and not coagulation, plays the basic role in the formation of the aerosol. Since the calculated concentration in the cloud formed by the flash is still great (about  $10^{11}/\text{cm}^3$ ), coagulation still takes place in the aerosol that is not yet cooled, and therefore it is not accompanied by the coalescence of particles. An aerosol generator is described in [41] in which cooling of the vapor-gas flow also takes place as a result of two processes--adiabatic expansion and mixing with a cold gas. In this instrument a hot gas-vapor stream is passed at a high rate through a nozzle into a cold gas. It was possible to obtain by this method rather monodispersed aerosols of selenium, without nuclei, with particle dimensions of 600 to 2,600 Å.

#### 54. HDA Production by Chemical Reactions in Gas Phase

Such processes as thermal and photochemical decomposition of carbonyl vapors, thermal hydrolysis of the vapors of metal chlorides and silicon tetrachloride, thermal destruction of hydrocarbons, have long been used on industrial scales for the production, through the aerosol state, of highly dispersed metal powders and their oxides, carbon black and Aerosil. Pertaining to all these processes is a vast amount of patent literature, examination of which extends beyond the scope of this review. Therefore we will discuss only a few works, the authors of which focus their attention on the mechanism of formation of aerosols during these processes. The dispersion of aerosols, metals and their oxides obtained in the works discussed below was characterized by a specific sediment area measured by the BET method.

Photolysis of the vapors of iron pentacarbonyl in the presence of oxygen has been used repeatedly for the production of aerosols [57-62]. It has been learned [61] that one quantum of light causes the separation of one CO molecule from the carbonyl complex, after which the  $\text{Fe}_2(\text{CO})_9$  complex is formed, which is oxidized in the presence of  $\text{O}_2$  to  $\text{Fe}_2\text{O}_3$ .

Kogan [63] used these reactions for the production of "molecular condensation nuclei". The process of the formation of  $\text{Fe}_2\text{O}_3$  was analyzed in depth [64]. It was established that as the time of illumination of a mixture of nitrogen and the vapors of iron pentacarbonyl by a mercury lamp is increased by 0.1 to 6 seconds the degree of decomposition of the latter increases from 10 to 100%. After illumination the nonreactive carbonyl was absorbed by passing the aerosol through a layer of activated charcoal, which reduced the effect of autocatalytic decomposition of the carbonyl on the surface of the particles. At a carbonyl concentration of  $36.2 \text{ g/cm}^3$  and degree of decomposition 10 to 100% it was possible to produce in this manner HDA with an average particle dimension of 22 to 82 Å.

The production of the aerosols of metal oxides during thermal hydrolysis of the vapors of their chlorides was investigated by a group of French researchers [65, 66] who fed a hydrogen burner with oxygen saturated with these vapors. The concentration of the chlorides varied from 3 to 12 mg/l, the temperature of the oxygen-hydrogen flame was 1,600 to 3,000°K. The average particle dimension of the precipitates of the HDA varied from 100 to 1,200 Å and decreased as the vapor concentration was reduced. More highly dispersed aerosols were obtained in the flame with the highest temperature of 1,500°K than in the flame measuring 3,000°K, but these aerosols were coarser than at 1,900°K. At high temperatures the dispersion is reduced, probably because of the agglutination of particles during coagulation; at exceedingly low temperatures hydrolysis takes place slowly and, accordingly, the rate of nucleation is lower. The coarsest particles were formed in the largest flame, and this is understandable considering that the rate of cooling of a submerged jet is reduced when its diameter is increased.

Zakutinskiy and Blyakher [67] analyzed thermal hydrolysis of  $\text{AlCl}_3$  vapor during mixing of a stream of nitrogen containing this vapor with air saturated with water vapor. Hydrolysis took place at temperatures between 400 and 450°C. Here, more highly dispersed aerosols were formed than during hydrolysis in a flame--at chloride concentrations of 5 to 30 mg/l the average particle dimension was 50 to 400 Å. Obviously the low temperatures at which Zakutinskiy and Blyakher worked precluded the agglutination of the particles and resulted in greater dispersion than in works [65, 66].

A review of works pertaining to the production of carbon black and Aerosil can be found in [68, 69], and the formation of HDA by radiolysis of gaseous hydrocarbons is discussed in [70].

Fuks and Oshman [71] described production of  $\text{H}_2\text{SO}_4$  HDA by mixing, in a capillary T-pipe, flows of air containing  $\text{SO}_3$  and  $\text{H}_2\text{O}$ . Investigation of the dispersion of these aerosols is described in [7].

## §5. Production of Dispersed HDA

The atomization of liquids produces particles of various dimensions including extremely fine particles. However, a real HDA that does not contain coarse particles at all or contains only a few coarse particles cannot be obtained by atomization. Likewise, HDA cannot be obtained by the atomization of polydispersed powders, since due to strong adhesion among the fine particles total deaggregation of such powders is impossible. By atomizing extremely dilute solutions and drying the droplets of the latter, however, it is possible to produce HDA from a dissolved substance. This method was used [72] for the generation of aerosols of different salts with an average particle dimension of 100 to 1,000 Å. Aerosols with an average particle dimension of 600 Å were obtained by the atomization [73] of salt solutions with a concentration of ~0.1%, separation of large droplets by bubbling and subsequent drying of the droplets. In modification of the LaMer generator, known as the Rapaport-Vaynshtok generator, was used [74] for the production of monodispersed particles of dioctylphthalate measuring  $\approx 400$  Å. The dioctylphthalate solution obtained by mechanical atomization in a methanol fog was passed through a heater, whereupon evaporation of both components took place. Then the gas-vapor mixture was passed through an air cooler, whereupon the vapors condensed on the walls, or remained in the vapor phase, and the dioctylphthalate vapors condensed on the walls and on the nonvolatile sediments of the vaporized particles that served as the seeds. The dimension of the particles obtained could be varied by changing the concentration of dioctylphthalate in solution.

The production of monodispersed aerosol with a particle dimension  $r = 320$  Å by atomization of a virus culture is described in [75].

In connection with the development of research on the creation of the electric aerosol motors and energy converters reports have appeared concerning the possibility of atomizing liquid cesium in a strong electrical field in a vacuum, forming particles measuring  $\approx 40$  Å [76]. Although these particles are suspended not in the gas medium, but in rarefied cesium vapors, the stated system can be conditionally classified as an aerosol. It is interesting to note that electrostatic atomization of liquids at normal pressure does not produce particles measuring  $< 2,000$  Å [77].

## CHAPTER II

### HDA INVESTIGATION METHODS

#### §6. Investigation of HDA in a Suspended State

Due to differences in the properties of aerosols with particle dimensions less than  $1,000 \text{ \AA}$  from those of coarser systems investigation methods also differ. HDA investigation methods can be broken down into two groups--investigations in suspended state and investigations based on measurement of the rate of sedimentation of the particles or investigation of the sediments.

Since the minimum dimension of particles visible under the ultra-microscope under normal illumination conditions is  $\sim 1,000 \text{ \AA}$  and the intensity of diffusion of light in HDA, according to the Rayleigh law, diminishes very rapidly as particle dimension decreases, HDA has very little optical density if only the concentration is not very high, and in the latter case they very rapidly coagulate and become coarsely dispersed. Therefore, in order to use the optical investigation methods on HDA it has to be enlarged by means of condensation on vapor particles of some other substance. For instance, in the adiabatic counters of Aytken and Shol'ts [78], long used by geophysists for determination of the concentration of condensation nuclei, the particles are enlarged by condensation of water vapor on them. The aerosol is admitted into a cylindrical chamber containing humid air. Expansion is brought about manually with the aid of a piston and is accompanied by adiabatic cooling and condensation of the supersaturated vapor. The water droplets formed by condensation on the particles settle out on a glass plate and are counted with the aid of a magnifying glass.

The degree of supersaturation created in such counters is usually sufficient for the detection of nonhygroscopic particles with a dimension exceeding  $100 \text{ \AA}$ .

The precise determination of concentration of even smaller particles is extremely difficult, even by increasing the degree of supersaturation, due to the diffusion sedimentation of particles on the walls of the counter chamber and the sample dosing apparatus during the taking of the sample and during the time period preceding expansion. Nolan and Pollak devised a photoelectric adiabatic counter [79-81], in which the fog that is formed does not settle out on the floor and the concentration of the particles is determined on the basis of light diffusion or extinction in the fog with the aid of a photoelectric sensor. This type of counter was initially calibrated with an Aiken counter, with the result that all errors contributed by the latter were also transmitted to the automatic counter. In the literature [81, 82] it described a counter designed for calibration purposes, in which the concentration of aggregated

particles was determined by means of stereo microphotography in the suspended state, thanks to which certain deficiencies of the Aytken counter were eliminated, although the principal source of errors--diffusion losses of fine particles, remained. Early modifications of the photoelectric counter had insufficient reproducibility and displayed a tendency toward reading drift in time [83], but eventually these deficiencies were eliminated [84]. It is noteworthy that calibration of the counter depends on temperature and pressure [85, 88]. The optical density of the fog [85] is related to its calculated concentration  $n$  by the empirical relation  $E \approx n^{0.46} M^{0.54}$ , where  $M$  is the mass of the vapor condensed per unit volume. Other instruments based on this principle are described by Vertsar [86] and Rich [87].

A number of authors have described automatic adiabatic counters in which expansion takes place at a rather high frequency--up to 5 times per second [89-90]. Here, the residence time of the aerosol in the chamber and connecting lines is reduced and diffusion losses should also have been decreased. However, such a high frequency of expansions inevitably leads to turbulization of the aerosol flow when fed into the chamber, which can increase the losses. In concluding this review of adiabatic counters it should be pointed out that they are hardly useful in investigations of particles measuring less than 100 Å due to the above-mentioned losses.

We know of flow instruments designed for counting with aggregation, in which diffusion chambers are used for the purpose of creating supersaturation [91-93]. With these, however, it is possible to create only low supersaturation, sufficient for detecting only rather large particles, approximately with  $d > 400$  Å, and the flow rates of the aerosol in these chambers are quite low.

LaMer developed the original flow method of enlarging liquid particles [43, 94-95]. Fogs of dibutylphthalate and sulphuric acid were passed over water and toluene, respectively. After a very short time the composition of the droplets goes into equilibrium with the vapor phase and the droplets enlarge correspondingly and are investigated by optical methods so that in addition to the calculated concentration it is also possible to find the dimensions of the original particles with the aid of simple calculations.

In [96] particles were enlarged by means of condensation of water vapor on them during mixing of flows of HDA and a hot vapor-gas mixture.

The method of flow enlargement of HDA proposed by Kogan and Burnasheva [97] turned out to be exceptionally successful. In the KUST enlarger which they designed (see Figure 1) a flow of cold HDA is mixed in a

conical diffusor with a flow of hot gas containing the vapors of a high-boiling liquid, for instance dibutylphthalate. The flows enter the diffusor coaxially--the hot vapor-gas mixture is fed to the center and the enlarged HDA is admitted on the periphery. During turbulent mixing of the flows supersaturation occurs, the degree of which can be controlled by the flow ratio, absolute flow rates, temperature in the vaporizer of the instrument, width of the annular gap through which the HDA enters the diffusor, and also by the choice of the working liquid. As a result of enlargement a stable monodispersed aerosol is obtained with an average particle dimension of a few tenths of a micron, which can be investigated by ordinary optical methods. The remarkable feature of the instrument is the independence of the dimension of the enlarged particles on the counted HDA concentration. This is explained by the fact that much of the vapor is condensed not into volume, but on the walls of the diffusor, and the actual supersaturation of the vapor in the instrument, and consequently, the dimension of the particles formed, are determined basically by condensation on this surface. In an improved version of the instrument, the KUST-4 [63] the upper concentration limit at which it has no effect on the dimension of the enlarged particles is  $\sim 10^5/\text{cm}^3$ . Owing to this property of the instrument the relative HDA concentrations can be determined with the aid of a nephelometer without preliminary calibration. Kogan managed with this instrument to detect even individual molecules of certain substances [63].

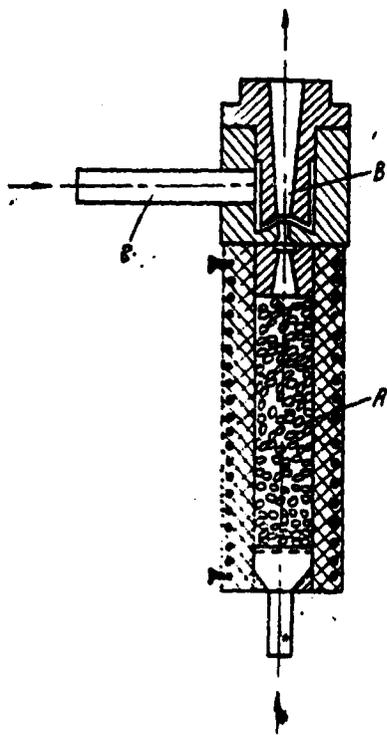


Figure 1. Diagram of KUST Instrument.

Measurement of light diffusion by enlarged and nonenlarged aerosols makes it possible to determine the average particle dimension of HDA exceeding 400 Å if its counted concentration is sufficiently high to ensure measurable light diffusion [97].

The question of the magnitude of particle losses during enlargement in the KUST instrument was discussed [98, 47]. For this purpose a flow enlarger was used, in which HDA was admitted into the diffusor axially, rather than peripherally as in the KUST instrument, while the hot gas-vapor mixture was admitted along the walls, with the result that diffusion losses were eliminated. By comparing the concentrations of the enlarged aerosols obtained in both instruments it was shown that the losses of NaCl particles measuring 50, 90 and 200 Å in the KUST instrument were 33, 17 and 10%. Unfortunately the modified enlarger produced less monodispersed aerosols and the particle dimension depended somewhat on their concentration.

Aytken [99] first measured the activity spectrum of condensation nuclei and Nolan [100] found that supersaturation required for detection of particles in his counter could be used for determination of their dimensions. Later on, in [101], this method was used for evaluating the particle dimensions of NaCl. The "chemical" diffusion chamber, in which one of the walls is moistened with water and the other with an HCl solution [101] can be used for creating low vapor supersaturation. With this chamber it is possible to achieve supersaturations in the 0.01-1% range with an accuracy of 0.01%. It was shown [103, 72] that the relative humidity at which particles of various mineral salts measuring 200 Å begin to enlarge is close to that calculated with the aid of the widely accepted thermodynamics relations. By this method it is obviously possible to determine the average dimension or even distribution of particles with respect to dimensions in aerosols consisting of one specific substance with a known wettability and hygroscopic properties. However, distribution with respect to dimensions cannot be found from the activity spectrum of aerosol particles of unknown composition [104]. The theory of detecting aerosol particles in a diffusion chamber was developed by Buykov [105, 106].

The dimension of uncharged particles is measured in [107] on the basis of their capture coefficient of gaseous ions. This coefficient can be found from measurements of the reduction of ion concentration when the investigated aerosol is admitted into a bipolar ionic atmosphere. Here, however, it is necessary to determine by independent method the counting concentration of the aerosol. Considering even that the dependence of the capture coefficient on particle dimension is not yet well defined, the possibilities of this method are unquestionable.

A flame counter was used [108, 109] for determination of the counting concentrations of aerosols from substances whose vapors produce strong illumination at high temperature, for instance, the salts of sodium or

lithium. In this device the aerosol enters the colorless flame of a hydrogen burner. The passing of the aerosol particles through the flame is accompanied by flares, which are recorded by a photomultiplier. A modification of this instrument, described in [110], permits the recording of NaCl particles larger than 400 Å. The upper limit of the counting concentration determined by this method is limited by the error resulting from coincidence, and is therefore not very high.

Recently the narrow angle diffusion of x-rays, by means of which it is possible to determine the distribution of particles with respect to dimensions, has been used for investigation of highly dispersed suspensions. It is logical to expect that this method will be used in the near future for concentrated HDA, for instance, for investigation of the process of their formation under stationary conditions.

#### §7. HDA Investigation Methods Based on Articulate Sedimentation

Of the various methods of this group, we will first discuss methods of determining the "electrical mobility" of particles, i.e., their rate of motion in an electric field with a voltage of 1 V/cm. The classical method of determining electrical mobility (concentration) of gaseous ions is the passing of ionized gas through a condenser and measurement of the current flowing through the latter as a function of the applied voltage, and was first used by Lanzheven [111] to investigation of heavy ions, i.e., charged particles of atmospheric aerosols. Since in HDA with  $d < 600 \text{ \AA}$  there are practically no particles with a charge greater than 1 elemental charge (see p. 62), it is possible to calculate from the electrical mobility spectrum of particles in such aerosols the distribution of charged particles with respect to dimensions. Since the percent of charged particles, generally speaking, increases with their dimension it is impossible by this method to find the distribution of all particles in HDA with respect to dimensions. Thus, this method, strictly speaking, is applicable only to monodispersed aerosols. Nevertheless, due to its simplicity it is used extensively in investigation of atmospheric aerosols. In [112] this method was used for analyzing HDA of sulphuric acid. Israel [113] contributed greatly to the development of this method.

In a similar method HDA samples are placed in the chamber of a Nolan-Pollak counter, in which there are flat electrodes with a potential difference applied to them [114]. The concentration of particles that remain in the condenser after various intervals of time, i.e., the kinetics of diminution of aerosol concentration is measured, after which particle distribution with respect to electrical mobilities and the percent of uncharged particles are calculated. Here it is necessary to disregard the diffusion sedimentation of uncharged particles on the condenser walls which in the case of very fine particles can lead to considerable errors.

After determining the percent of uncharged particles in a more or less monodispersed HDA under conditions of a charge in a bipolar ionic atmosphere it is possible to calculate particle dimension. The Boltzmann equation can be used in the first approximation for this purpose: for the fraction of uncharged particles is obtained the expression

$$\frac{n_0}{n_0 + n_1 + n_2 + n_3 + \dots} = \frac{1}{1 + 2 \exp [e^2 / 2akT] + 2 \exp [(2e)^2 / 2akT]} \quad (7.1)$$

where  $n_0$  is the concentration of uncharged particles,  $n_1$  is the concentration of particles with  $\pm 1$  elemental charge, etc. According to the latest data [115] an exponential formula analogous to the Boltzmann equation properly describes the distribution of charges in HDA with a particle radius  $>200 \text{ \AA}$ . For more highly dispersed aerosols the concentration of charged particles under stationary conditions can be calculated only approximately (see §12). This method, advanced by Wright [116] and improved by Rich [117] can be used for particles of any dimension, but is not valid for polydispersed aerosols. In the latter case a certain equivalent radius  $a_e$  can be calculated from formula (7.1). As shown in [118], the ratio of  $a_e$  to the arithmetic mean radius is greater the higher the polydispersion of the aerosol and can be used as a measure of the latter.

When using methods based on measurement of the stationary distribution of electrical charges it must be borne in mind that a certain time is required to achieve such a state, in particular, under conditions of natural ionization tens of hours may be necessary for this purpose [119].

The diffusion method of determining the dimensions of HDA particles first used by Townsend for measurement of the mobility of gaseous ions, is extremely fruitful. This method was first used on aerosols by Nolan [120] and Radushkavich [121]. The method is based on measurement of the diffusion sedimentation of particles on the walls during laminar flow of the aerosol through a channel of circular or rectangular cross-section. The passage of the aerosol, i.e., the ratio  $n/n_0$  of concentrations at the outlet and inlet of the channel can be precisely calculated theoretically and the diffusion coefficient  $D$  of particles, related to their mobility  $B$  (rate of motion under the influence of a constant force of 1 dine) by the relation  $D = kTB$  (see §10 concerning the dependence of  $B$  on particle dimension) can be determined from passage measurements. The formulas for diffusion sedimentation (and for the mathematically equivalent problem-- heat transfer in a channel) were derived by several authors in the form of

series. In a cylindrical channel, in the case of nonsteady diffusion (when on the particle concentration profile in the channel cross-section there is a plateau with initial concentration) passage is expressed by the formula [122]

$$n/n_0 = 1 - 2,56\mu^{2/3} + 1,2\mu + 0,177\mu^{4/3} \div \dots \quad (7.2)$$

where  $\mu = Ds/R^2\bar{v}$ ,  $x$  is the length of the channel,  $R$  is its radius,  $\bar{v}$  is the mean linear flow rate. For the steady diffusion state ( $\mu > 0.05$ ) [173]

$$n/n_0 = 0,819 \exp(-3,657\mu) + 0,097 \exp(-22,3\mu) + 0,032 \exp(-5,7\mu). \quad (7.3)$$

In a plane-parallel channel (in whose cross-section length greatly exceeds width  $2h$ ) passage in both states is quite accurately expressed by the De Marcus equation [124]

$$n/n_0 = 0,9149 \exp(-1,885\mu) + 0,0592 \exp(-22,33\mu) + 0,0258 \exp(-151,8\mu). \quad (7.4)$$

in which  $\mu = Dx/h^2\bar{v}$ .

The numerical integration of the equation of diffusion in a plane-parallel channel, carried out in [125] on a computer, yielded a result that agrees satisfactorily with the analytical solution of De Marcus.

In practice an aerosol is often passed through a system of parallel channels--an apparatus for which Rodebash [126] offered the name "diffusion battery". In this case the expression for  $\mu$  should contain in the numerator a factor equal to the number of channels. The rate of sedimentation of HDA particles is so low that it is not necessary when working with HDA to place the battery in the vertical position. The above formulas are valid for sedimentation of monodispersed aerosols, but actually all aerosols are polydispersed and when they flow through a channel it is primarily the finest, most mobile particles that settle out. Therefore, the apparent diffusion coefficient of a polydispersed aerosol, which can be calculated with the aid of the above equations, increases as the characteristic parameter  $\gamma = \mu/D$  increases. Hence, diffusion measurements are valuable only when they make it possible to find the diffusion coefficient that corresponds to a certain average particle dimension for the entire dimension distribution of the particles. At the present time,

there are four methods used for processing diffusion experimental data<sup>1</sup>, about which it is possible to find the parameters of particle dimension distribution. Pollak and Metniks [127] worked out the so-called exhaustion method, which consists in the following. If we assume that an aerosol is a mixture of several monodispersed fractions characterized by increasing diffusion coefficients  $D_1, D_2, \dots, D_i$  and fractions of calculating concentrations  $p_1, p_2, \dots, p_i$ , we can show that

$$\exp(-KD'/\bar{v}) = \sum_i p_i \exp(-KD_i/\bar{v}), \quad (7.5)$$

where  $D'$  is the empirical diffusion coefficient corresponding to flow rate  $\bar{v}$ ;  $K$  is a coefficient that includes the structural parameters of the battery in accordance with equation (7.3) or (7.4). When  $\bar{v} \rightarrow \infty$ , by expanding the coefficients in (7.5) into a series we obtain  $D' =$

$$= \sum_i p_i D_i, \text{ i.e., to } \bar{v} \rightarrow \infty \text{ corresponds the mean weighted value } D \text{ of the}$$

mixture of the fractions. When  $\bar{v} \rightarrow 0$  only the term corresponding to the fraction with the smallest  $D_1$  remains in formula (7.5). Therefore, by extrapolating the experimental function  $n/n_0 = f(y)$  to  $\bar{v} \rightarrow 0$  we can determine  $D_1$  and  $p_1$ . After subtracting  $p_1$  from the total number of particles we can make the conversion, determining how the function  $f(y)$  looked for the aerosol from which was excluded the first fraction, then extrapolate again to  $\bar{v} = 0$ , find  $D_2$  and  $p_2$ , etc.

This method has been used in works of the Irish school [128, 129]. Equation (7.5) was derived with consideration only of the first term in the right-hand side of equation (7.4); more awkward expressions are obtained with consideration of the second term. Nolen and Scott [130]

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<sup>1</sup>Stechkina [163] has just offered the fifth method of determining the parameters of articulate dimension distribution, based on the asymptotic expansion of the integrals in (7.6) with respect to the small parameter  $\beta_g$ . Using the analytical expressions obtained in this work it is possible to find  $\alpha$  and  $\beta_g$  from measurements of  $D$  for two values of  $\bar{v}$ .

delved into the problem of the influence of the number of fractions removed on the accuracy of the method and found that the correct representation of the real dimension distribution can be reached by making the aerosol of at least nine fractions. Together with this, this method yields low accuracy, despite cumbersome calculations, due to the need for repeated extrapolation. Fuchs, Stechkina and Starosel'skiy [131] calculated on a computer the values of the integral diffusive passage as a function of  $n/n_0 = f(y)$  for aerosols of the logarithmically normal distribution with respect to dimensions  $g(a)$  from the formula (see 7.4)

$$n/n_0 = 0.9149 \int_0^{\infty} g(a) \exp[-D(a)y] da + \\ - 0.059 \int_0^{\infty} g(a) \exp[-D'(a)y] da + \dots \quad (7.6)$$

With systems of curves  $f(y)$  corresponding to a certain mean geometrical particle radius  $a_g$  in the range between 10 and 1,000 Å and to the logarithms of standard geometrical deviation  $\sigma_g$  from 0 to 0.4 were plotted. The Millikena-Knudsen equation was used for particle mobility (see 59). It should be pointed out that logarithmically normal distribution was observed in aerosols of most varied origin. The curves  $n/n_0 = f(y)$  borrowed from [131] are illustrated in Figure 2. For practical use of this "method of best approximation" the calculation curves, constructed in the same scale on tracing paper, are superimposed on the experimental data plotted on coordinates  $(n/n_0, \log y)$ , and are moved along the abscissa until the best matching of the experimental points with one of the calculation curves is achieved. In this way  $a_g$  is determined.  $\bar{D}$  is found from the amount of displacement along the  $\log y$  axis required for matching with the family of curves corresponding to the given  $a_g$ .

From the theoretical point of view, Tumi used the most logical approach [132], but it turned out to be unsuccessful. By transforming equations (7.3) or (7.4) for the case of a polydispersed aerosol and deriving an expression analogous to (7.7), he showed that the experimental dependence  $n/n_0 = f(y)$  can be equated to a converging series of functions of the form  $g(a)A_i e^{-a_i y}$ , which are the Laplace transforms of the desired distribution function with respect to dimensions  $g(a)$ . Therefore, the latter can be found with the aid of the inverse Laplace transform. Theoretically, this method can be used for aerosols with any unknown

dimension distribution. As shown by calculations carried out by Tumi himself with the aid of a computer, however, if for a given  $g(a)$   $f(y)$  is calculated and then if conversion is made back to  $g(a)$ , the latter will differ substantially from the first  $g(a)$ . The error associated with this circumstance increases considerably if the function  $f(y)$  is found inaccurately as the result of imperfect measurements. Only with an accuracy in the determination of passage in the entire range of measurements, corresponding to errors  $\leq 0.5\%$  can good results be obtained with the aid of this method. Since such accuracy is usually unattainable, the Tumi method, obviously, is suitable only for estimation of the width of dimension distribution in extremely polydispersed aerosols, for instance in atmospheric condensation nuclei.

Nolen and Scott [130] derived an approximate relation for determination of particle distribution parameters in terms of the diffusion coefficients

$$D' = \bar{D} - \sigma^2 / 2\bar{v} \quad (7.7)$$

Here  $\bar{D}$  is the value that corresponds to  $\bar{a}$ ,  $D'$  is the value found from experiment at the rate  $\bar{v}$ ,  $\sigma$  is standard deviation of  $D$ . By determining  $D$  for two values of  $\bar{v}$  it is possible to find  $\bar{D}$  and  $\sigma$  from which the conversion can be made to the average dimension and dispersion of particle dimensions. Metniks [133] recently compared by the calculation method three methods for determining the distribution parameters of particles with respect to dimensions--exhaustion method, best approximation method and the Nolen-Scott method. Metniks considered the Laplace inverse transform method [132] practically impossible. The values of  $n/n_0 = f(y)$  found by the calculation method from various particle dimension distributions were processed by all three methods. Here, the calculations were formed for distributions in which the number of particles was proportional  $a^{-1}$ ,  $a^{-3}$  and  $e^{-a}$ , and also for normal, logarithmically normal, and a certain bimodal distribution. It was explained that the curves calculated in [131] satisfactorily approximated the function  $f(y)$  for all these distributions. The exhaustion method also produced good results, but the Nolen-Scott method turned out to be suitable only in the case of normal and logarithmically normal distribution, and even then its accuracy was less than that of the other two methods. The advantages of the best approximation method over the exhaustion method are shown in the work of Nolen and Scott [130].

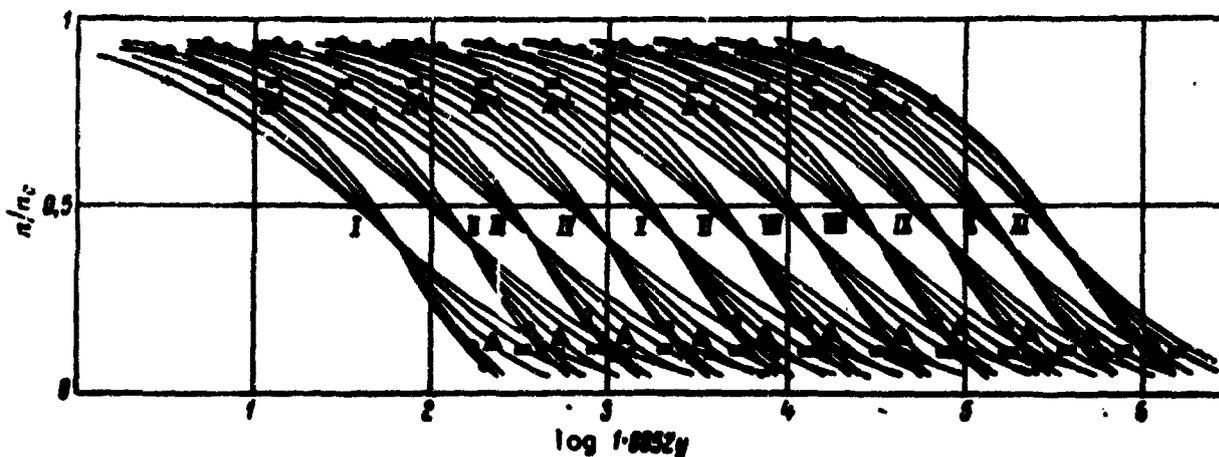


Figure 2. Diffusive Sedimentation of Polydispersed Aerosols in Plane Parallel Channel. Curves, N, a, A: I, 10; II, 16; III, 25; IV, 40; V, 63; VI, 100; VII, 160; VIII, 250; IX, 400; X, 630; XI, 1,000; Symbols:  $\log \beta_g$  -o- o-a:  $\Delta$  -a:  $\square$  -a:  $\times$  -a

The solutions of equation (7.2) and (7.4) of diffusion from a laminar flow were found on the assumption that a parabolic flow profile is established in the very beginning of the channel. Meanwhile, this profile is established, for instance, in a circular tube only at a distance of  $0.05 R.Re$  from the inlet, where  $Re$  is the Reynolds number. Thorough examination shows that diffusion sedimentation in the intake part is much greater than in the case of a parabolic flow profile. Since the diffusion parameter corresponding to the end of the intake part is  $\mu_{in} \approx 0.1 D/v$ , where  $v$  is the kinematic viscosity of the gas, the reduction in passage through the battery caused by this condition increases as the diffusion coefficient increases. This effect is of practical importance only in terms of extremely highly dispersed aerosols with a particle radius  $\leq 10 \text{ \AA}$ . Thomas [134] attempted to eliminate the error caused by the intake effect by measuring the passage ratio  $n/n_0$  in two batteries having lengths of 47 and 5 cm and by assuming this ratio to be equal to passage through a battery 42 cm in length. However, this approach can produce considerable error in the region of small  $\mu$  due to the fact that passage can only approximately be considered an exponential function of length. When the influence of the second and third terms in equations (7.3) and (7.4) is great passage through batteries of length  $l_1$  and  $l_2$  is not equal to passage through a battery of length  $l_1 + l_2$ .

This error was recognized by Thomas himself [136]. Nevertheless, Tumi [137], in order to find the points corresponding to various  $y$ , passed an aerosol through the same battery a different number of times. This method involves the same error, since passage through a battery of length  $L$  is different from the square of passage through a battery of length  $L/2$ .

An empirical correction for the intake effect was used in [40]. This correction is suitable for investigation of aerosols with a small dimension distribution width. In the case of a monodispersed aerosol the values of  $D$  calculated experimentally for various  $y$  should coincide. For practical purposes, however,  $D$  depends on  $y$  even in the case of a monodispersed aerosol, and this dependence is attributed to more intensive sedimentation of particles in the intake section in comparison with sedimentation in the established flow. If  $y$  is changed not as the result of a change in the velocity of flow through the battery, but by using a battery of different length, then the relative effect of the intake effect will diminish as the battery length is increased and the absolute value of the effect will be the same for measurements for all  $y$ . Therefore, the intake effect can be evaluated by comparing passage measured in batteries of various lengths. As seen in Figure 2 the limbs of the calculation curves for  $\log \beta_g = 1.0$  and  $1.26$  for values  $n/n_0 >$

$> 0.45$  coincide. This permits evaluation of the magnitude of the intake effect even for aerosols possessing some polydispersion, but in this case it is necessary to compare passages that exceed  $0.45$ . It was explained in [40] that this correction is notable only for extremely highly dispersed aerosols; nevertheless, even for aerosols with  $\bar{a} = 7-10 \text{ \AA}$  the correction factor for passage through very short batteries (through which passages were measured in the range of  $0.85-0.9$ ) did not exceed  $1.05-1.02^1$ .

Experimental determination of the function  $f(y)$  is made by measuring the concentrations of consolidated aerosol before and after the battery. In the works of Nolen and Pollak and coworkers their adiabatic counter was used for this purpose, and in the works of the authors of the present review [40, 42, 98] a KUST flow enlarger [97] (see pp. 20-21) was used in combination with a photoelectric nephelometer. Sometimes the radiography

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<sup>1</sup>The equation of the diffusion of particles to the walls of a circular channel during the process of establishing a parabolic profile was recently solved by calculation methods [163]. The additional sedimentation of particles in the intake section was 2% with a Schmidt number  $Sc = \nu/D = 10$  and 5% for  $Sc = 0.9$ . This agrees satisfactorily with the empirical correction introduced in [40].

of filters through which is passed an aerosol, passed and not passed through a battery, is used for determination of  $n/n_0$  during work with radioactive aerosols [138, 139]. In [139] the measurements of the total radioactivity of the filters were compared with the concentrations of the particles measured by an adiabatic counter before and after the battery, and it was shown that the radiographic method yields two to three times lower values of  $D$ . This is understandable, since the radioactivity of activated decay products of the emanations of aerosol particles increases with dimension. The distribution of activity in the sediment on the walls of the diffusion channel was measured [140] in order to determine the diffusion coefficient of the decay products of radon. The diffusion coefficients were calculated from the measurement results with the aid of Berezhniy's solution [141] of the equation that describes sedimentation of products formed inside the diffusion channel itself.

When designing diffusion batteries it is necessary to bear in mind that it is impossible to create a "universal" battery suitable for the entire range of dimensions of HDA, since their diffusion coefficient varies from about  $10^{-1}$  to about  $10^{-5}$   $\text{cm}^2/\text{sec}$ . To find the required values of  $u$  in the entire dimension range it would be necessary to vary by four orders the flow rate through the batter, which is inconceivable, since at high velocities the hydraulic resistance increases greatly and at small velocities the air attributed to convection currents increases. Calculations and personal experience of the authors of this review indicate that it is advisable to use slit batteries for particles larger than 200  $\text{\AA}$ , and for dimensions of the order of 10  $\text{\AA}$ --batteries made of cylindrical channels. A set of batteries of different length, consisting of eight tubes, each one 6 mm in diameter, was used in [198] for investigation of aerosols in the particulate dimension range of 14-60  $\text{\AA}$ , and for particles measuring 60 to 200  $\text{\AA}$ , a set of 60-channel batteries consisting of tubes measuring 1.4 mm in diameter. Generally speaking it is not advisable to use a large number of small diameter tubes for batteries, but rather a few wide tubes, since in this case there is a greater possibility of expansion of the range of values  $y$  of the battery due to change in the flow velocity. The use of a set of batteries of different lengths for determination of the function  $f(y)$  makes it possible to exclude error in the measurement of flow velocity, since all measurements are made at the same velocity, and facilitates the introduction of the correction factor for the intake effect.

As regards errors that may occur with the diffusion method, instead of the above-mentioned intake effect we should point out the acceleration of sedimentation of charged particles on the channel walls due to mirror forces. Calculations [142, 143] indicate that this effect is negligibly small if the particles carry no more than one elemental charge, but can be considerable in a case of large charges. In checking the diffusion

method with the aid of a monodispersed aerosol obtained from polystyrene latex, Migo and Uiffen [144] showed that the correct results can be obtained only when grounded metallic batteries are used. Latex particles undoubtedly could carry large charges. It was revealed in [40] that if the investigated aerosol had a higher temperature than the battery wall, precipitation of small  $\mu$  was greater than in isothermic conditions, obviously as a result of thermophoresis and convective transfer. When working with exceedingly highly dispersed aerosols it is important to keep the losses in the connections constant during measurements in batteries of different lengths. For this purpose the stopcocks were omitted in [40] and the difference in the length of the battery was compensated by moving the KUST instrument on a dolly. The latter measure is necessitated by the fact that according to the observations of the authors and also of Nolen and Kaffel [145] the sedimentation of particles takes place much more vigorously in curved rubber tubes than in straight ones due to the electrical charges created by the bending of the tubes.

In addition to Migo and Uiffen, Thomae [135] also checked the diffusion method, comparing the results of the optical and diffusion determinations of particle dimensions in the 1,000--3,000 Å range and obtaining satisfactory agreement. The slight discrepancies noted can be attributed completely to incorrect compensation of the intake effect. For coarser particles the diffusion method is unsatisfactory due to an increase in sedimentation, which cannot be eliminated, even by using vertical batteries.

Essentially, the diffusion method can be used not only in channels, but also in any system of bodies that permit theoretical calculations of the diffusive sedimentation of particles from a flow, for instance, in a model of fibrous filters consisting of a system of parallel cylindrical, randomly arranged fibers oriented perpendicular to the flow. The passage of HDA through such a model is expressed by the formula

$$n/n_0 = \exp(-2\xi\eta H/\pi R_f), \quad (7.8)$$

where  $\xi$  is the fraction of the volume filled by the fibers;  $H$  is the thickness of the model,  $R_f$  is fiber radius,  $\eta$  is the coefficient of capture of the particles by the fibers, expressed by the theoretical formula [146]

$$\eta = 2,9K^{0.7} Pe^{-0.5} + 0,624Pe^{-1}$$

where  $Pe = 2R_f \bar{V} / D$ ,  $K = 1/2 \ln \xi + \xi - \xi^2 - 0,75$ ,  $\bar{V}$  is the average flow velocity

in the model. Formula (7.9) is in satisfactory agreement with experimental data [147] on the passage of monodispersed HDA with  $\bar{a} = 18-80$  Å through model filters (see Figure 3). The diffusion coefficients of the particle were determined in these experiments with the aid of diffusion batteries. The advantage of this version of the diffusion method is the absence of input effects.

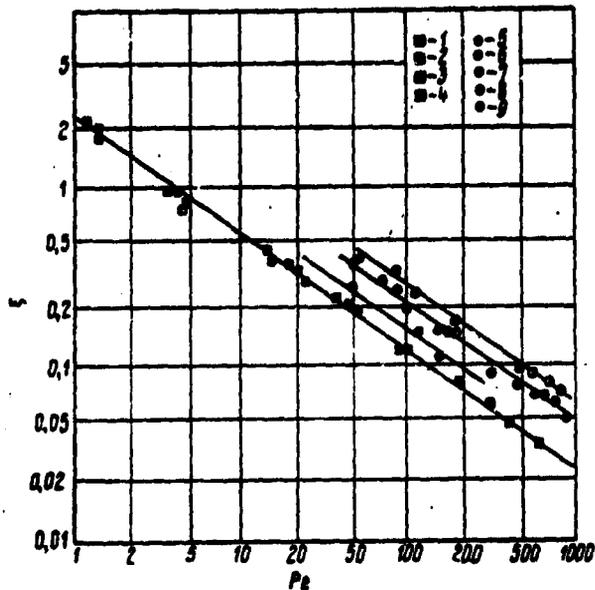


Figure 3. Capture Coefficients of Diffusive Sedimentation of Particles in Model Filter with Checkerboard Distribution of Cylinders:

Theoretical curves

I- $\xi = 0.01$ ; II- $\xi = 0.05$ ; III- $\xi = 0.135$ ;  
IV- $\xi = 0.27$ .

Mean particle radius

a, Å: 1-15; 2-18; 3-60; 4-60;  
5-70; 6-41; 7-70; 8-55

In [148] the diffusion method was combined with the determination of the number of charged particles: for the latter purpose the diffusion battery was used as a plane-parallel condenser. Measurement of the percent of charged particles in stationary conditions makes it possible to determine the "equivalent" dimension of aerosol particles (see p. 29), from diffusion measurements it is possible to determine some average particle dimension and the ratio between these two average values can characterize qualitatively polydispersion. The general idea of this method is valid, but since the values of  $D$ , measured by the diffusion method, depend on  $\gamma$ , the result thus obtained will depend both on the parameters of the aerosol and on the measurement conditions.

In some works [149, 150] the so-called "static diffusion method" was used. In this method the change in the concentration of an aerosol at rest in a cylindrical or spherical vessel in time is traced. For particles with a dimension of about 10 Å this method is unsuitable, since such particles settle out in time not exceeding a few seconds, and for coarser particles it becomes less accurate than the dynamic method due to errors attributed to convection.

Labeyri [151] offers a method for investigation of aerosols, including highly dispersed aerosols, based on their radioactivation by

adding radon. After settling out of the decay products on aerosol particles these latter can be trapped in a filter, after which the filter is subjected to radiographic analysis and the number of particles counted.

In conclusion, we will examine HDA investigation methods based on their preliminary sedimentation. The method of investigating highly dispersed sediments does not depend on the method by which they are obtained. Therefore, it is not useful here to examine in detail, for instance, the electron microscopic methods, since they are discussed in an abundance of special literature. We will confine ourselves here only to examination of specific moments that occur during investigation of aerosol sediments. The chief condition here is the representation of the sample, i.e., the method of particle sedimentation need not be selective. Usually thermal precipitators, designs of which insure sampling of representative samples were described in [152] and [153], are employed for sampling. The most representative samples are obtained with thermal precipitators with a moving wire [154]. Sometimes electro-precipitators are also used for sedimentation. Since classification of particles takes place to some extent in these instruments during the motion of aerosol along the sedimentation electrode, it is necessary to analyze samples taken at various points of the electrode. The electroprecipitators are used almost exclusively for investigation of aerosol sediments by means of the BET method, x-ray diffraction analysis and other methods.

An ingenious electrostatic precipitator design is described in [155]. A jet of charged HDA in coronal discharge is admitted to a laminar flow between plane-parallel or coaxial electrodes. Classification during sedimentation is a result of the fact that the rate of displacement of the particles to sedimentation electrode is proportional to the charge and inversely proportional to the resistance coefficients of a particle.

Electron microscopy is an extremely important HDA investigation method, since it permits direct determination of the dimensions and shapes of aerosol particles and also of the count concentration of HDA. However, the use of electron microscopy for analysis of HDA involves certain difficulties which increase by measure of reduction of particle dimension, caused by the fusing and evaporation of particles by the electron beam, and also by reduction in image contrast due to increased particle transparency. The known electron microscopic methods--shading of particles by vacuum sublimation of heavy metals, shading of replicas, sandwich method [156, 157], are of limited benefit, since during analysis of extremely fine particles the thickness of the shaded layer becomes commensurate with the particle dimension. Therefore, it is not surprising that although many authors have analyzed sediments of particles with a dimension approaching the limit resolution of the electron microscope [32, 44, 45], as illustrations for their articles they prefer to use photographs of particles measuring between 100 and 1,000 Å. It is

pointed out in [47] that it is impossible to take sharp photographs of NaCl particles measuring less than 200 Å, but in [158] it is not explained that Pt and Ni particles measuring less than 100 Å are either transparent to electrons, or evaporate rapidly under their influence. The authors of the present review are not successful with the aid of the electron microscope, with a resolution limit of 15 Å, to investigate the structure of MoO<sub>3</sub> aggregates consisting of individual particles measuring about 100 Å (as was done by the BET method). The problem of microscopy of liquid particles should be considered unsolved. In those cases where it is possible to gather weighable quantities of aerosol sediment, the average particle dimension can be calculated from the specific area of the sediment, determined by any of the common methods. If after coagulation the particles did not stick together or unite, but loose aggregates were formed, the dimension of the former, noncoagulated aerosol can be determined from the specific surface of the sediment, although the formation of solid aggregates and particularly their agglomeration can lead to overestimation of particle dimension calculated in this way. In [65, 66] the results of the BET method were compared with the electron microscopic analyses and it was established that in determination of the particle dimension of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> sediments obtained by the interaction of the vapors of the chlorides of these metals with water vapor at 1,600-2,000°C, both methods yield similar results.

The results of both methods also agree satisfactorily [37] with respect to sediments of aerosols of oxides of the metals obtained in an electric arc. On the other hand, the reduction has been noted [47, 48] in the specific area of the sediments of NaCl and nickel HDA, which can be a serious source of errors, particularly if there is a lengthy time lapse between sediment production and its analysis.

Membrane filters are also used for HDA analysis [159-161]. Cartright [162] for electron microscopy, used the method of producing relics from particles precipitated on membrane filters. For analysis of radioactive aerosols radiography of filters, including membrane filters, is often employed. Sometimes membrane filters are used for detection of highly dispersed particles possessing icing activity. For this purpose the filter, after the settling out on it of these particles, is immersed in a super-cooled sugar solution and ice crystals form on the active particles. Here, preliminary determination of the icing background of the filter is required, since each filter contains two to three centers that possess activity of this type.

In concluding our discussion of HDA investigation methods we might point out that the present methods insure reliable determination of all parameters of HDA consisting of solid particles.

## CHAPTER III

### HDA PROPERTIES

#### §8. Transfer Process in HDA. General Comments

The processes of mass, energy, pulse and charge transfer from a medium to particles and back are of fundamental importance in aerosol physics. The character of these processes is governed by the Knudsen number  $Kn = \lambda/a$ . When  $Kn \rightarrow 0$  these processes are described accurately by the equations of thermoconductance, diffusion and hydrodynamics of continua. When  $Kn \rightarrow \infty$  particles do not violate Maxwellian distribution of the velocities of gas molecules moving toward the particles, and for molecules moving away from the particles the distribution function is relatively simple to find. Therefore, transfer processes in this "free molecular" mode are expressed through simple formulas, derived from molecular kinetic theory of gases.

Otherwise, we are dealing with transfer at intermediate Knudsen numbers: here the theory is fraught with tremendous mathematical difficulties. For quite a long time the "stitching" method was used to solve this problem: it was assumed that transfer in the immediate vicinity of a particle occurs in the free molecular mode and starting at some distance of the order of  $\lambda$  from the surface of the particle, according to the equations of transfer in continua. Although in certain cases a stitching method produced rather good agreement with experimental data it essentially cannot be accurate. Nevertheless, this method alone is still used for charge transfer.

The rigorous calculations of the rate of transfer for intermediate Knudsen numbers can be based only on the solution of the Boltzmann kinetic equation, and this, in turn, is possible only after some simplification, (linearization) of the latter. The simplest linearization method advanced independently by Welander and Bkhatnagar and coworkers, and described in the ensuing section, permitted the successful solution of several problems of theoretical physics. Brock and Willis used this method in conjunction with "Knudsen iteration" for transfer phenomena in aerosols. Knudsen iteration consists in expansion of distribution function  $f$  into a series by powers  $Kn^{-1}$

$$f = f_0 + f_1 Kn^{-1} + \dots \quad (8.1)$$

where  $f_0$  is the Maxwell distribution function. By substituting this expression into the linearized Boltzmann equation the above-stated authors were able to solve it, retaining only the first two terms in the expansion,

and thereby found the function  $f_1$ , i.e., the first approximation to the distribution function, and hence determined the transfer rate or flow of the corresponding value to a spherical particle. The formulas thus derived or flows, have the form

$$\Phi = \Phi_k / (1 + \lambda Kn^{-1}) \quad (8.2)$$

where  $\Phi_k$  is flow in the free molecular mode and  $\lambda$  is sum constant. It is noteworthy that formulas of this form can be accurate only when  $Kn^{-1} \ll 1$ .

Considerable progress has been made in recent years in the theory of transfer processes at intermediate Knudsen numbers, and this progress has been made by researchers having very little to do with HDA. Sakhin, working on the theory of transfer and absorption of neutrons in nuclear reactors, made an accurate calculation of the rate of mass transfer to a sphere for all Knudsen numbers using the so-called integral equation. Since transfer processes at high and intermediate Knudsen numbers are of great importance in the aerospace industry, this problem attracted the attention of many theoreticians. Using the variation method developed by Cherchin'yanin Pagani, they were able to make an accurate calculation of the heat flux to a spherical particle and the resistance of the medium to its motion for all Knudsen numbers, and the calculation results agree very satisfactorily with the experimental data.

Naturally, in works related to the aerospace industry a great deal of attention is devoted to transfer processes at high particle velocities in relation to the medium and high temperature and concentration gradients. In the present review we will examine only the case of low values, in particular, low velocities in comparison with the thermal velocity of molecules.

We should mention, finally, that in the theory of the processes of transfer to particles it is inevitably necessary to proceed on the basis of the concept of mean free path of gas molecules. At the same time this concept is generally not used in modern theory of transfer processes in a gas volume, chiefly because it is somewhat lacking in definition. In essence, in the theory of transfer to particles  $\lambda$  should be regarded not as the mean distance traveled by molecules between consecutive collisions, but as the mean effective free path  $\lambda_{eff}$ , which may differ for the various transfer phenomena. Thus,  $\lambda_{eff}$  for mass transfer is the average distance that separates a molecule from the initial position at the moment when its velocity vector becomes independent of the initial velocity vector. In heat transfer  $\lambda_{eff}$  is the distance at which the

molecule acquires the average temperature of the surrounding gas, and in moment transfer is the distance at which the molecule acquires the average (i.e., hydrodynamic) gas velocity. Without going into detailed analysis of this question, it may be stated, for instance, that in view of the incomplete transfer of energy corresponding to the inner degrees of freedom of molecules in collisions,  $\lambda_{\text{eff}}$  for heat transfer may be greater than for moment transfer. Up to now this important fact has been taken into account only in the work of Lord and Harbor [165].

### 39. Mass Transfer in HDA: Evaporation and Condensation Growth of Particles

Evaporation and condensation growth of particles play an extremely important role in the formation and life of aerosols and have been the object of numerous theoretical and experimental investigations. Therefore, we will examine these processes at some length. When  $Kn \rightarrow 0$  they are accurately described by the diffusion equation. Ordinarily an extremely idealized process--evaporation (or growth) of a single spherical particle at rest in an infinite volume, not interacting with a gas particle, is examined. The problem is especially simplified if the partial pressure of the vapor is substantially less than that of the gas. With this assumption, collisions among vapor molecules can be disregarded and the process can be assumed to be quasistationary, since the relaxation time of the vapor concentration distribution around the particle is much less than the total particle evaporation time [166]. In the ensuing discussion we will consider this case alone.

At a sufficiently great distance from a particle vapor transfer takes place by diffusion. The difference of equation of stationary vapor diffusion from a sphere or to it has the form

$$\rho^2 \frac{dn}{d\rho} = I, \quad (9.1)$$

where  $n$  is vapor concentration at distance  $\rho$  from the center of the sphere;  $I$  is the constant found from the boundary condition on the surface of the sphere.

We will examine the two simplest cases--evaporation of particle in a medium not containing vapor and condensation on a "black", i.e., one that absorbs all vapor molecules that strike it, sphere. Since in these cases  $n$  is proportional to the concentration  $n_s$  of the saturated vapor of the particle or to the concentration  $n_\infty$  of the vapor, respectively, for  $\rho \rightarrow \infty$ , by integrating (9.1) we obtain in the former case

$$n = -\delta n_s / \rho, \quad (9.2)$$

and in the latter,

$$n = n_\infty (1 - \delta/\rho), \quad (9.3)$$

where  $\delta$  is a constant, positive for condensation and negative for evaporation. Diffusive flow to the sphere (and from it) is expressed by the formulas

$$\Phi = 4\pi D \delta n_\infty \quad \text{and} \quad \Phi = 4\pi D \delta n_s, \quad (9.4)$$

If the vapor concentration at infinity during evaporation is not equal to zero, but to  $n_\infty$ , then it is necessary in all corresponding formulas to replace  $n$  by  $n - n_\infty$  and  $n_s$  by  $n_s - n_\infty$ . The analogous substitution must be made for condensation on a particle with a vapor pressure not equal to zero, but to  $n_s$ .

All these equations are valid for any Knudsen number, but only at a great distance from the sphere. When  $Kn \rightarrow 0$ , however, vapor transfer is of a diffusive character all the way to the very surface of the sphere, the boundary condition for evaporation will be  $n_{\rho=a} = n_s$ , and for condensation on a black sphere  $n_{\rho=a} = 0$ . Thus, in the case  $\delta = \pm a$  and (9.4) also converts to the familiar Maxwell formulas

$$\Phi_e = 4\pi D a n_\infty \quad \text{or} \quad \Phi_c = 4\pi D a n_s, \quad (9.5)$$

We will note that when  $Kn \rightarrow 0$  the mass transfer rate is independent of the evaporation (condensation) coefficient  $\alpha_c$ . Otherwise, according to recently published data [167],  $\alpha_c$  is close to unity for all liquids.

When  $Kn \rightarrow \infty$  the rate of evaporation of a particle (when  $n = 0$ ) and condensation on it ( $n_s = 0$ ) is expressed by the Knudsen formula for evaporation in a vacuum

$$\Phi_e = \pi a^2 \alpha_c \bar{V}_v n_s \quad \text{or} \quad \Phi_c = \pi a^2 \alpha_c \bar{V}_v n_\infty, \quad (9.6)$$

where  $\bar{V}_v$  is the average velocity of thermal motion of vapor molecules. The indices  $c$  and  $k$  denote transfer in the continuous and in the free molecular modes. We will note that

$$\Phi_e/\Phi_s = \frac{4}{3} \text{Kn} a_c^{-1} \quad (9.7)$$

As already pointed out, the first attempts to solve the problem of the evaporation of particles at intermediate Knudsen numbers amounted to the stitching together of the free molecular and diffusion flows. In a number of works [168-170] the flows were stitched together directly on the surface of the particle, i.e., it was assumed that the diffusion equation was valid all the way to the very surface. The formula obtained by this method

$$\Phi = \Phi_s (1 - \frac{1}{2} \text{Kn}) + \Phi_e (1 + \frac{4}{3} \text{Kn}^{-1}) \quad (9.8)$$

gives the correct functional dependence of  $\Phi$  on  $\text{Kn}$ , but considerably overstated coefficients for  $\text{Kn}$  and  $\text{Kn}^{-1}$ .

In the "boundary sphere" method [166] the stitching was made on the surface of a sphere surrounding a particle, consisting of the surface of the particle at a distance  $\beta L$ , by which, on the average, evaporating vapor molecules, having traveled distance  $L$ , are separated from the particle (when  $\text{Kn} \rightarrow 0 \beta = 1/2$  and when  $\text{Kn} \rightarrow \infty \beta = 1$ ). The formula for this is

$$\Phi = \frac{\Phi_e}{\frac{4}{3} \text{Kn} a_c + 1/(1 + \beta \text{Kn})}$$

When  $\text{Kn} \ll 1$  and  $a_c = 1$

$$\Phi = \frac{\Phi_e}{1 + \frac{1}{3} \text{Kn}} \quad (9.9)$$

which is quite close to the accurate expression, although when  $\text{Kn} \gg 1$  an incorrect functional dependence is obtained:

$$\Phi = \Phi_e / (1 + 3\text{Kn}^{-2}/4) \quad (9.10)$$

Thus, we see that the stitching methods do not produce the proper results. We will also note that the "universal" interpolation formula of Sherman [171], which he proposed for several transfer processes

$$\Phi = \Phi_s (1 - \Phi_e/\Phi_s) + \Phi_e (1 + \Phi_s/\Phi_e) \quad (9.11)$$

coincides with formula (9.7) when  $a_c = 1$ .

The rigorous solution of the problem of particle evaporation at intermediate Kn numbers is possible only on the basis of the Boltzmann kinetic equation. Under the above assumption of low vapor concentration in comparison with the concentration of the gas, the distribution function of the molecules of the latter will be only slightly perturbed by collisions by vapor molecules and it can be assumed to satisfactorily approximate the Maxwellian concentration all the way to the very surface of the particle. However, for vapor molecules the Maxwellian distribution occurs only at a great distance, compared to  $l$ , from the surface of the particle. In the case of a "black" sphere, at its very surface the projections of the velocities of all vapor molecules onto the normal to the surface are directed toward the latter, i.e., here the distribution function is described by a single "half" of Maxwellian distribution directed toward the sphere. By measure of distance from the sphere this asymmetry of distribution gradually vanishes. Vapor transfer at a great distance from the sphere is purely diffusive, i.e., determined by the vapor concentration gradient. By measures of convergence upon the sphere the diffusive vapor flow acquires the flow attributed to the asymmetry of the distribution function and only this latter flow remains at the surface of the sphere.

The chief difficulty in the solution of the kinetic equation is the collision integrals it contains. These integrals determine the change in the number of molecules in a given elemental volume and which possess a given velocity vector, due to their collisions with other molecules that happen to be in this volume. This difficulty is attributed principally to the fact that beneath the integrand are the products of the distribution functions. The collision integral was replaced in [172, 173] by the simple expression  $v(f_0 - f) dt$ , where  $dt$  is an element of space,  $f$  is the distribution function in this space,  $f_0$  is the Maxwellian distribution function,  $v$  is thenumber of molecular collisions per unit time in space (in our case, collisions among molecules of the vapor and gas). This method was used successfully for the solution of several physical problems, in particular, by Melander for calculating heat transfer from a heated cylinder of radius commensurate with  $l$ .

In the problem at hand, this method takes on a graphic physical meaning: instead of examining in detail the changes in the distribution function of the vapor molecules, caused by their collisions with the gas molecules (according to what was said above, collisions between vapor molecules can be disregarded), we will assume that during these collisions the vapor molecules acquire Maxwellian (isotropic) velocity distribution, which gas molecules possess. It should be stressed that this assumption is valid only when the mass ratio of the vapor and gas molecules is  $m_v/m_g \rightarrow 0$ . Otherwise there may be some persistence in the

velocities of the vapor molecules and their velocity distribution may not be completely isotropic after collisions.

Brock [174, 175] used this method of linearization of the kinetic equation in combination with the Knudsen iteration for the theory of mass transfer for  $Kn \gg 1$ . Brock gives only the final formula without the calculations. The correction factor of this formula contains the mean free path of gas molecules  $l_g$ . Since all formulas presented in this section contain the mean free path  $l_v$  of vapor molecules, which appear as an impurity in the gas, we transformed Brock's formula with the aid of the well-known gas kinetics formulas

$$l_g = (\sqrt{2} \pi n_g d_g^2)^{-1}, \quad (9.12)$$

$$l_v = (\pi n_g d_{vg}^2 [1 + m_v/m_g])^{-1}, \quad (9.13)$$

where the indices v and g pertain to the vapor and gas; d denotes molecular diameter and  $d_{vg} = 0.5(d_v + d_g)$ . Here the Brock formula acquires the following form:

$$\Phi = \Phi_0 (1 - \alpha_0 0.807 \sqrt{2} 6Kn^{-1}), \quad (9.14)$$

where  $\theta$  is a factor related to persistence of the vapor molecules and is equal to 0.295, 0.150 and 0.115 for  $m_v/m_g = 0, 1$  and 9, respectively.

As is clear from the foregoing, and as Brock himself points out, these calculations, strictly speaking, are applicable only in the case  $m_v/m_g \rightarrow \infty$ , when formula (9.14) can be represented in the form (when  $\alpha_c = 1$ ):

$$\Phi = \Phi_0 (1 - 0.12Kn^{-1}) \approx \Phi_0 (1 + 0.42Kn^{-1}). \quad (9.15)$$

As we will learn below, this formula yields the more or less correct value of  $\Phi$  when  $Kn \gg 1$ .

We can find the lower boundary for the coefficient for  $Kn^{-1}$  from elementary considerations. We calculate the probability that the evaporated molecule will fly off to distance  $l$  along the normal to the particle surface, there to collide with a gas molecule and return to the particle

without experiencing new collisions. This probability, obviously, is proportional to the ratio of the solid angle, at which the particle is seen at the given distance, to 4. Taking into account the distribution of free paths of the molecules on their way to and from the particle, we find for the mean probability of return of the molecules the expression

$$\bar{W}_1 = \frac{1}{2l_v} \int_0^{\infty} \left( 1 - \frac{\sqrt{\frac{x^2}{a^2} + 2\frac{x}{a}}}{2\left(1 + \frac{x}{a}\right)} \right) e^{-2x/l} v dx. \quad (9.16)$$

When  $Kn^{-1}$  is small,  $\bar{W}_1 = 0.285 Kn^{-1}$ . If we were to consider the fact that the molecules evaporate from the surface not normally, but at various angles, then we would find a somewhat higher value for  $\bar{W}_1$ . The total probability of return of the molecules to particle  $W$ , is obviously greater than  $W_1$ . Since the rate of evaporation of a particle with consideration of returns is  $\phi_k = (1 - W)$ , obviously the true coefficient for  $Kn^{-1}$  should in any case be greater than 0.285.

When the diffusion of vapor molecules is nonisotropic and their velocities persist after collisions, the probability of their return to the particle after the first collision is obviously less, and this is increasingly true as persistence increases, i.e., the larger the ratio  $m_v/m_g$ . Thus, in formula (9.16)  $l$  should be defined as an "effective" mean free path of molecules  $l_{\text{eff}}$  (see §8). Formula (9.15), obviously, should be handled in a like manner until someone manages to develop an accurate transfer theory that takes into account velocity persistence. As has been shown [176],

$$l_{\text{eff}} = l_v (m_v/m_g + 1) / (1 + \beta), \quad (9.17)$$

where  $l_v$  is the mean distance traveled by vapor molecules between two collisions;  $\beta$  is the number, equal to 0, when  $m_v/m_g \rightarrow 0$ , which increases monotonically with  $m_v/m_g$  and reaches the value 1/3 when  $m_v/m_g \rightarrow \infty$ . It follows from (9.17) and (9.13) that

$$l_{\text{eff}} = (\sqrt{m_v/m_g + 1}) / (1 + \beta) \pi n_g d_g^2. \quad (9.18)$$

After replacing in the Meyer formula for the diffusion coefficient of a vapor in a gas

$$D_v = \bar{V}_v l_v / 3 \quad (9.19)$$

$l_v$  with  $l_{\text{eff}}$ , we obtain the Dzhin [176]

$$D_v = \frac{\bar{V}_v \sqrt{1 + m_v/m_g}}{3(1 + \beta) \pi n_g d_{vg}^2}, \quad (9.20)$$

which differs from the familiar Stefan-Maxwell formula only by a factor  $(1 + \beta)$  close to unity. Thus, in formula (9.15) it is easier to use the value  $l_v$  calculated from the coefficient of mutual diffusion of the vapor and gas according to formula (9.19).

The most accurate solution of the problem of mass transfer in aerosols at intermediate Knudsen numbers was found in the theory of neutron transfer. One of the most important problems of this theory is the so-called "Miln's spherical problem", i.e., calculation of a flux, to a black sphere, of neutrons, diffused isotropically by heavy atoms [177], is completely equivalent to the examined problem for the case  $m_v/m_g \rightarrow 0$ .

We will first assume that all vapor molecules possess the same absolute velocity, i.e., the distribution function contains only a single velocity vector. In this case the collision integrals were considerably simplified and several attempts were made to solve the kinetic equation. The most complete and accurate results were obtained by Sakhni [178], who based his work on the so-called integral equation and used in his calculations both analytical and mathematical methods.

The problem at hand is characterized by the fact that a "diffusion" approximation is often found instead of its accurate solution, i.e., vapor concentration distribution around a sphere, which satisfies diffusion equations (9.1-9.3), and for large  $\rho$  it coincides with the accurate distribution, and therefore gives the accurate magnitude of flux to a sphere according to formula (9.4). Usually, instead of the constant  $\delta$  in this formula, the "linearly extrapolated length", i.e., the expression

$$l = \frac{n_{\text{dif}}(a)}{l_v \left| \frac{dn_{\text{dif}}}{d\rho} \right|_{\rho=a}}, \quad (9.21)$$

is calculated. The geometric meaning of this expression is clearly shown in Figure 4, which depicts concentration distribution according to the accurate solution and according to diffusion approximation for  $Kn = 0.5$ , by Sakhni's calculations. As seen in Figure 4, at a distance  $\geq \delta$  from the surface of the sphere the concentration according to diffusion approximation is quite close to its accurate value, and here mass transfer is almost exclusively the result of diffusion; for shorter distances, however, the diffusion equation is not valid. The same is also true of other Knudsen numbers.

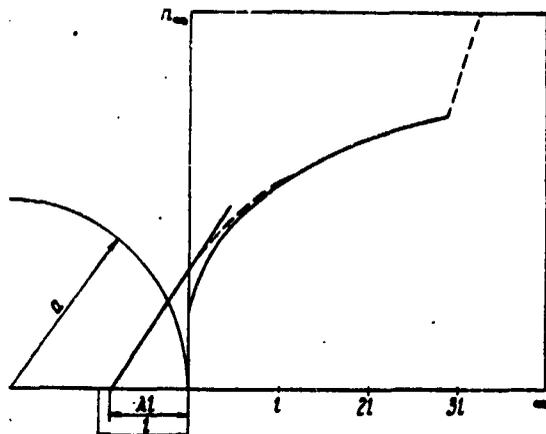


Figure 4. Concentration Distribution Near Absorbing Sphere.

By comparing formulas (9.3) to (9.21), we find that  $\delta = a/(1 + \lambda Kn)$  and formula (9.4) acquires the form

$$\Phi = \frac{4\pi a D n_{\infty}}{1 + \lambda Kn} = \frac{\Phi_c}{1 + \lambda Kn} \quad (9.22)$$

The values of  $\lambda$  as calculated by Sakhni are presented in Table 1. According to the author himself, their accuracy is about 0.3%.

TABLE 1. VALUES OF COEFFICIENT  $\lambda$  ACCORDING TO SAKHNI.

$Kn^{-1}$	$\lambda$	$Kn^{-1}$	$\lambda$
0	1,333	1,30	0,997
0,1	1,296	1,50	0,972
0,2	1,353	2,0	0,925
0,5	1,155	2,5	0,892
0,7	1,104	5,0	0,815
1,0	1,043	$\infty$	0,710

$Kn \ll 1$  we obtain from (9.22)

$$\Phi = \Phi_c (1 + 0,710Kn). \quad (9.23)$$

For  $Kn \gg 1$   $\lambda$  must be expressed in accordance with the table in the form  $\lambda = 1.333 - 0.37 Kn^{-1}$  and  $D$  is replaced by  $\sqrt{2}l/3$ . Consequently, we obtain

$$\Phi = \Phi_c / (1 + 0,472Kn^{-1}), \quad (9.24)$$

which is close to Brock's formula (9.15).

Since it is not convenient to use the table in calculations of evaporation kinetics, it can be replaced by the interpolation formula

$$\lambda = \frac{1,333 + 0,71Kn^{-1}}{1 + Kn^{-1}}. \quad (9.25)$$

The maximum deviation of values calculated according to this formula from those presented in Table 1 is 2 to 6%. When the evaporation time of a particle is calculated using formula (9.25) we obtain an integral that is easily taken as a rational function of  $a$ .

Since the average absolute velocity  $\bar{v}_v$  molecules does not figure in the derivation of formula (9.24), or in calculation of  $\lambda$ , the above limitation--assumption of equal absolute velocity of all molecules, is discarded: the velocity distribution can be anything desired, including Maxwellian, and only the retention of  $\bar{v}_v$  during collisions and diffusion isotropy, i.e., the condition  $m_v/m_g \rightarrow 0$ , are required. Since  $l$  depends on  $\bar{v}_v$ , the average  $l_{eff}$  should be used in (9.22).

The theory of neutron transfer also takes into account the case of persistence of their velocities, although Miln's spherical problem has no solution that takes into account persistence, and in lack of a better approach, persistence should be taken into account, as indicated above on p. 49.

Since the condensation coefficient  $\alpha_c$  for certain solids may be less than 1, the case of a "grey" sphere, that absorbs only the fraction  $\alpha_c$  of vapor molecules colliding with it, must be examined. It is obvious

that a grey sphere is equivalent to one that possesses some natural vapor tension and  $\alpha_c = 1$ . Through  $n_-$  and  $n_+$  we will denote the concentrations of vapor molecules at the surface of the sphere, moving to and from it. Obviously,

$$n_+ = n_- (1 - \alpha_c) \quad (9.26)$$

The flux of molecules to and from the sphere can be expressed through the formulas

$$\phi_+ = 2\pi a^2 \bar{v} n_- = 2\pi a^2 \bar{v} n_+ + 2\pi a^2 \bar{v} (n_- - n_+), \quad (9.27)$$

$$\phi_- = 2\pi a^2 \bar{v} n_+ \quad (9.28)$$

However, such fluxes will also occur in the case of a sphere that possesses vapor tension  $2n_+$ , when  $\alpha_c = 1$  and for the resultant flux to the sphere, equal to

$$\Phi_{gr} = 2\pi a^2 \bar{v} (n_- - n_+). \quad (9.29)$$

Thus these two spheres are equivalent, i.e., the vapor concentration distributions around them are identical. As follows from what was stated on p. 50, the resultant flux may also be described in the form

$$\Phi_{gr} = 4\pi a D (n_\infty - 2n_-) (1 + \lambda a). \quad (9.30)$$

By excluding  $n_+$  from formulas (9.26) and (9.29) and setting  $\phi_{gr}$  and  $\phi'_{gr}$  equal we can find the expression for  $n_-$  and, hence, the formula for the flux to a grey sphere

$$\Phi_{gr} = \frac{\Phi_r}{1 + \left[ \lambda + \frac{4(1-\alpha_c)}{3\alpha_c} \right] Kn}, \quad (9.31)$$

which Smirnov derived by a different method [179].

We will return to the problem of the effect of capillary forces on the evaporation of flying particles in §15.

Proceeding now to comparison of the theory outlined here with the sparse existing experimental data, we notice that direct measurements of the rate of evaporation of HDA particles are extremely difficult to make, and therefore it is necessary to work with low gas pressures (to increase  $L$ ). All that can be said of the known tests of Bradley and coworkers [180] and Monchik and Rayse [181] is that these tests do not contradict the above theory, although their accuracy is too low for solution of the remaining unsolved problem of the influence of the persistence of vapor molecules on the mass transfer rate.

Calculation of the growth or evaporation of aerosol particles under actual conditions requires that the heat emissions of phase transition, influence of particle motion and other factors be taken into account. Several papers have been published in connection with examination of these questions. Brock calculated the condensation flux to a particle moving in the free molecular mode [182], and in another of his works [175], calculated the liberation of the heat of condensation during free molecular growth. Using the Belander-Bkhatnagar model, he also studied the problem of nonstationary particle growth rate for intermediate Knudsen numbers. Smirnov [184] found expressions for growth rate with evaporation rate of particles with consideration of the heat of phase transition and a number of secondary factors based on the results of neutron transfer theory. Kang Sang-wook [185] used the boundary sphere method not only for calculating the growth rate of particles, but also for calculating the rate of dissipation of the heat of condensation.

The theoretical results obtained from his formula were compared with Weatherstone's tests on the condensation of mercury vapors in a jet [186] although this comparison did not produce any conclusions concerning the validity of the formula derived in [185].

Noteworthy also are methods of calculating the rate of evaporation of a collection of aerosol particles, proposed by Okuyama and Zung [187] and rate of premolecular evaporation of water droplets sprayed into a greatly rarefied plasma [188].

In concluding, we will note briefly the adsorption of gases and vapors on HDA particles. Obviously, the equations for the vapor condensing on particles may also be used for describing adsorption kinetics. The only difference should be the dependence of the probability of adhesion on the amount of material sorbed, i.e., on the degree of coating of the surface by the adsorbate. The over-all process of the adsorption of vapors on aerosol particles can be calculated if the desorption kinetics of the material are known.

The boundary sphere method was used in [189] for evaluation of the rate of adsorption of iodine vapors by atmospheric condensation nuclei and it was found that iodine should be sorbed almost entirely within 30 seconds. In practice, however, due to simultaneous desorption, the

fraction of iodine bonded to the particles did not exceed 75% of the total amount of iodine in the atmosphere, and this value was reached only after 2 1/2 to 3 hours.

As regards the adsorption of the decay products of emanations, they almost entirely ionized [190]. Therefore the process of their capture should be described by the equations for the rate of charging of HDA particles by gaseous ions (see §12).

#### §10. Pulse Transfer in HDA: Resistance of Medium to Particle Motion

This process occupies a special place in the theory of transfer in aerosols, since only in this case do there exist accurate and completely reliable experimental data, furnished by Milligan [191], for oil droplets, and therefore accurate checking of the theoretical calculations is possible.

At sufficiently small Reynolds numbers the resistance of a medium is expressed, for  $Kn \rightarrow 0$  by the Stokes formula

$$F_c = 6\pi r \eta U, \quad (10.1)$$

where  $U$  is particle velocity,  $\eta$  is gas viscosity.

For  $Kn \rightarrow \infty$  Epstein [192] derived the following formula:

$$F_k = \frac{1}{\beta} \pi \rho n_c m_c a^2 \bar{v}_k U, \quad (10.2)$$

where  $\beta$  is a coefficient whose value depends on the mechanism by which molecules are reflected from a particle. In the case of total thermal accommodation and diffusion scattering of molecules  $\beta = 1 + \pi/8$ , and in the case of mirror reflection  $\beta = 1$ . By substituting in (10.2) the known expression for gas viscosity  $\eta = 0.499 \frac{n m v l}{g g g}$ , we may write (10.2) in the form

$$F_k = 6\pi r \eta U (A + Q) l, \quad (10.3)$$

where the value of  $A + Q$  has, in the two above-mentioned cases, the values 1.616 and 2.250. From (10.1) and (10.3) follows

$$F_c F_k = (A + Q) Kn. \quad (10.4)$$

Milliken expressed the results of his tests with oil droplets through the empirical equation

$$F = F_c \left[ 1 + A \frac{l}{a} + Q \frac{l}{a} \exp(-ba/l) \right]^{-1}, \quad (10.5)$$

in which  $A = 1.234$ ,  $Q = 0.414$  and  $b = 0.876$ . Obviously, in  $l/a = Kn \rightarrow \infty$  (10.5) is converted to (10.3). By comparing the theoretical values of  $A + Q$  with the experimental value 1.65, we may make the following formal conclusion: that a small part of the molecules is reflected from the surface of the droplets in the mirror fashion and that the rest of the molecules experience complete accommodation and are diffused.

The first attempt at a theoretical calculation of the resistance of a medium at intermediate Knudsen numbers was undertaken by Fuchs and Stechkina [193] using the boundary sphere method. On the basis of a number of incompletely substantiated assumptions, these authors derived the following formula for resistance to motion of oil droplets:

$$F/F_c = \left[ \frac{1}{1 + 0.42Kn} + 1.67Kn \right]^{-1}. \quad (10.6)$$

The values of  $F/F_c$  calculated from this formula differ by not more than 2% from Milliken's data.

By breaking down the collision integral in the kinematic equation in terms of Hermit's polynomials and using the Knudsen iteration, Liu and coworkers [194] derived the formula

$$F/F_c = 1 - 0.298Kn^{-1}. \quad (10.7)$$

By linearizing the kinetic equation as indicated in §9, Willis [195] using the Knudsen iteration, derived the expression

$$F/F_c = 1 - 0.366Kn^{-1}. \quad (10.8)$$

Chercignani and Pagani [196] solved transfer problems in the range of intermediate Knudsen numbers by a new method. After the linearization of the kinetic equation the authors constructed a functional from the functions that express the density of the gas, velocity of the molecules and temperature, and used the variation method to find the stationary value of the function. Here, the above-specified physical values acquire values that correspond to the solutions of the linearized equation, but the fluxes of pulse, heat, etc. are calculated directly from the stationary values of the functional. Using this method the authors were able to

solve an entire series of transfer problems in the systems with different geometry.

Recently, Cherciyani and Pagani [197] published a work in which the above method was used for the problem of the resistance of a medium to the motion of spheroidal particles. Their calculation results for spherical particles are depicted in Figure 5 as the dependence of  $F/F_k$  on  $Kn^{-1}$ . The calculations quite satisfactorily approximate the experimental formula (10.5); the slight difference between them, which never exceeds 2%, can be attributed to the fact that in the expression for  $F_k$  the authors used for the coefficient  $\beta$  the value  $1 + \pi/8$ , i.e., they assumed that all gas molecules experience total accommodation on the surface of particles, whereas in actuality a small portion of them is reflected in mirror fashion. The works of Cherciyani and Pagani doubtless have made an extremely important contribution to the theory of transfer phenomena at intermediate Knudsen numbers.

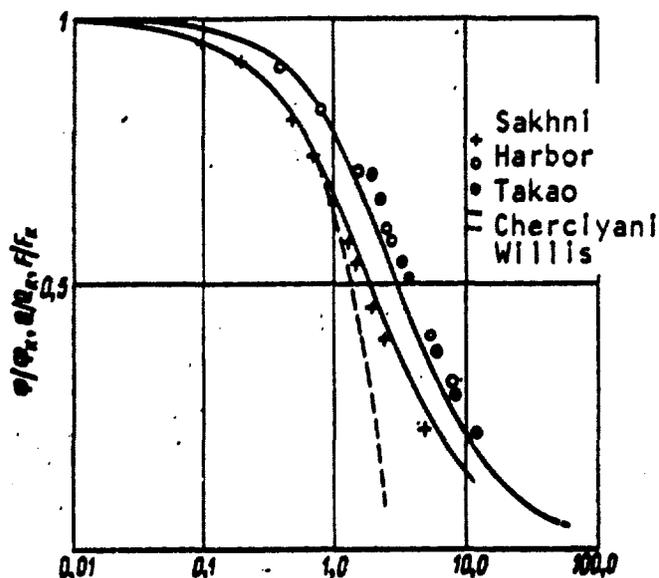


Figure 5. Kinetics of Transfer Processes at Intermediate Knudsen Numbers.

It is clear in Figure 5 that Willis' formula (10.8), as expected gives the correct values of  $F/F_k$  only approximately to  $Kn^{-1} \approx 0.5$ , while formula (10.7) is completely inaccurate. As regards the "universal" Sherman formula (see equation (9.11)),

$$F/F_k = \frac{1}{1 + F_k/F_c} \quad (10.9)$$

which can be represented through formula (10.4) as

$$F/F_k = \frac{1}{1 - \text{Kn}^{-1}(1 - Q)^{-1}} = \frac{1}{1 + 0.006\text{Kn}^{0.7}}$$

which then yields somewhat understated (up to 7%) values of  $F/F_k$ . It is extremely fortunate that the values of  $\phi/\phi_k$ , calculated according to Sakhni's data for mass transfer (from Table 1) with the aid of formula (9.7), as functions of  $\text{Kn}^{-1}$ , quite satisfactorily rely on the curve for pulse transfer, as seen in Figure 5. At the same time the curve for heat transfer lies somewhat higher.

Brock [198] derived quite a complex expression for the resistance of a medium to the motion of growing or evaporating particles at high Knudsen numbers, which undoubtedly will be of benefit for calculation of the formation of aerosols in rocket nozzles and influence of the particles formed on the flux properties.

### §11. Heat Transfer in HDA: Heating and Cooling of Particles

The importance of the process of heat transfer to particles from its surroundings lies primarily in the fact that the temperature of an evaporating or growing, due to condensation, particle differs from the temperature of the surrounding environment, and this fact, in the case of materials with notable vapor tension, has a considerable effect on the kinetics of evaporation and growth of particles.

For  $\text{Kn} \rightarrow 0$  the rate of heat transfer to a particle is expressed by a formula, derived in classical thermal conductance theory, analogous to (9.5),

$$Q_c = 4\pi a \chi \Delta T \quad (11.1)$$

where  $\chi$  is the heat transfer coefficient of the medium;  $\Delta T$  is the temperature difference between the medium and the particle. We will confine our examination to the simplest case where  $\Delta T$  is small compared to the absolute particle temperature  $T$ .

To derive the expression for heat flux to a particle when  $\text{Kn} \rightarrow \infty$  we will introduce, as in the derivation of formula (9.31), the indices + and - to denote molecules moving away from and toward a particle. From the

condition of material balance it follows that  $n_g^+ \bar{v}_g^+ = n_g^- \bar{v}_g^-$  or

$$n_g^+ \sqrt{T^+} = n_g^- \sqrt{T^-}. \quad (11.2)$$

The flux of molecules to a particle is (insert a) and the mean thermal energy of one molecule is  $c_v T^-$ , where  $c_v = 3/2k$  for monatomic and  $5/2k$  for diatomic gases. However, the energy flux to a particle cannot be found by multiplying these two values, since the greater the kinetic energy of molecules, the relatively more often they collide with the particles. The correct expression for energy flux [199] is of the form

$$I = \pi a^2 n_g^- \left( \frac{8kT^-}{\pi m_g} \right)^{1/2} \left( c_v + \frac{k}{2} \right) T^-. \quad (11.3)$$

The analogous expression (in which the - is replaced by the +) is also found for the energy flux carried away by the molecules, and the resultant flux is equal to the difference of these expressions:

$$Q_k = \pi a^2 \left( \frac{8k}{\pi m_g} \right)^{1/2} \left( c_v + \frac{k}{2} \right) n_g^- (T^-)^{3/2} - n_g^+ (T^+)^{3/2}. \quad (11.4)$$

We will introduce the coefficient of temperature accommodation of molecules  $\alpha_T = \Delta T / \Delta T$ , where  $\Delta T$  is the difference between the average temperature of molecules departing from particles and the temperature of the environment; obviously  $\Delta T = T^- - T^+$ . Assuming  $\Delta T / T$  to be a small value, we find from (11.4), using condition (11.2), the formula

$$Q_k = \pi a^2 \left( \frac{8k}{\pi m_g} \right)^{1/2} \left( c_v + \frac{k}{2} \right) n_g T^{3/2} \Delta T = \pi a^2 n_g \bar{v}_g \left( c_v + \frac{k}{2} \right) \alpha_T \Delta T. \quad (11.5)$$

We will now find the value of the ratio  $Q_c / Q_k$ . From the known formula for the thermal conductance of gases  $\chi = \epsilon n c_v / m_g$ , where  $\epsilon$  is the viscosity of the gas and the coefficient  $\epsilon$  is equal to 2.5 for monatomic and 1.9 for diatomic gases, and from the formula  $\eta = 0.5 n m_g \bar{v}_g l$ , we obtain

$$\gamma = 0,5 z c_v n_g \bar{u}_g l, \quad (11.6)$$

hence

$$Q_c/Q_k = 2z c_v Kn / \left( c_v + \frac{k}{2} \right) \alpha_T. \quad (11.7)$$

Thus, for monatomic gases  $Q_c/Q_k = 3.75 Kn \alpha_T^{-1}$ , and for diatomic gases  $Q_c/Q_k = 3.17 Kn \alpha_T^{-1}$ .

For an intermediate Knudsen number Springer and Psai [200] derived, using the boundary sphere method, the formula

$$Q/Q_c = \left[ \frac{1}{1+Kn} + BKn \alpha_T^{-1} \right]^{-1}, \quad (11.8)$$

where B - 3.75 for monatomic and 3.17 for diatomic gases. When  $Kn \rightarrow \infty$  this formula acquires the form  $Q/Q_c = (B Kn \alpha_T^{-1})^{-1}$ . Considering the expressions for  $Q_c/Q_k$ , we see that  $Q/Q_k \rightarrow 1$ , in this case as should be expected.

Using the moment method, Lees [201] found that for diatomic gases the formula

$$Q/Q_c = (1 + 2,5 Kn)^{-1}, \quad (11.9)$$

which is clearly unsuitable for large Knudsen numbers.

Sherman's universal formula has in this case the form

$$Q/Q_k = \frac{1}{1 + Q_k/Q_c} = \frac{1}{1 + \beta \alpha_T Kn^{-1}} \quad (11.10)$$

[see formula (11.7) concerning the value of  $\beta$ ].

The above-described Knudsen iteration method was used by Brock [202] for derivation of the formula

$$Q/Q_k = 1 - \alpha_T B Kn^{-1}, \quad (11.11)$$

where  $B = 0.153$  for monatomic and  $0.239$  for diatomic gases. Formulas of this type, as we have already stated, are valid only for large Knudsen numbers.

Cherchiani and Pagani [203] used the variation method mentioned in the preceding section (assuming  $\alpha_T = 1$ ) to calculate the values  $Q/Q_k$  for monatomic gases in the range of Knudsen numbers from  $0.0001$  to  $50$ . Figure 4 shows the curve plotted according to these data.

Up until just recently the only experimental determination of the rate of heat transfer to a sphere at low Reynolds numbers and at intermediate Knudsen numbers was made by Takao [204] who measured the kinetics of cooling of the heat glass sphere  $1.5$  cm in diameter, placed in a vessel measuring about  $1$  m, from which the air was exhausted to the desired residual pressure. All the above-cited authors compared the formulas which they derived (Takao himself also derived an extremely complex formula with Takao's data and they all found excellent coincidence. It should be pointed out that Takao expressed his results in the form of the dependence of  $Q/Q_c$  on Knudsen number. Generally speaking, however, Takao's data are sufficiently accurate only for small Knudsen numbers and are erroneous for  $Kn \geq 1$ , as indicated by the strong scattering of experimental points in this range. For  $Kn > 1$ , apparently, recently published results of Harbor [205], also in error, are more accurate.

Figure 5 shows, in addition to Cherchiani's curve, Brocks curve (11.11), which nearly coincides with it at large Knudsen numbers, and the experimental data of Harbor and Takao. Unfortunately, the values of  $\alpha_T$  in the test of Takao and Harbor are unknown, which makes it difficult to compare the theory with the experiment.

As already mentioned in §8, it is necessary in heat transfer calculations to use the mean free path of molecules specifically for this process, i.e.,  $l_h$ , rather than the generally accepted value for moment transfer  $l_m$ . According to the calculations of Lord and Harbor [165] for diatomic molecules,  $l_h/l_m \approx 1.6$ . If, however, Cherchiani's curve is related to  $l_m$  rather than to  $l_h$ , it must be displaced to the left in such a way as to reduce the abscissa by a factor of  $1.6$ . Then this curve will nearly coincide with the analogous curves for mass transfer and pulse transfer and we will have practically the same curve for all three processes.

§12. Charge Transfer in HDA: Charging and Discharging of Particles by Gas Ions

One of the most important physical processes in aerosols is charge transfer to particles by ions captured by them. It is noteworthy that until just recently we did not know the exact nature of a gas ion. The whole series of facts indicates that primary ions, formed when an electron separates from or combines with molecules of a gas, are united by the electrical forces of neutral molecules that possess constant dipole moment, forming aggregates. The electrical mobilities of atmospheric "bright" ions lie in the range from about  $0.5$  to  $2.5 \text{ cm}^2 \cdot \beta^{-1} \cdot \text{sec}^{-1}$ . Hence the number of molecules in ionic aggregates also varies substantially.

Since the expressions for the electrical mobility and coefficient of diffusion of ions [199]

$$B = \frac{3}{8} \pi^{1/2} l_i e \left( \frac{m_g + m_i}{m_g m_i k T} \right)^{1/2}, \quad (12.1)$$

$$D = \frac{3}{8} \pi^{1/2} l_i \left[ \frac{(m_g + m_i) k T}{m_g m_i} \right]^{1/2}. \quad (12.2)$$

contain both mean free path of ions  $l_i$  and their mass  $m_i$  ( $m_g$  is the mass of neutral gas molecules), we can determine  $l_i$  only by assigning a certain value to  $m_i$ . If we assume  $m_i = m_g$  and take for mobility the mean value  $B = 1.4 \text{ cm}^2 \cdot \beta^{-1} \cdot \text{sec}^{-1}$ , then in air of  $20^\circ$  and at normal pressure we will have  $l_i = 1.3 \cdot 10^{-6} \text{ cm}$ , and for the mean thermal velocity  $v_i = 4.62 \cdot 10^4 \text{ cm/sec}$ .

If, however, like Young [206] we assume that  $m_i/m_g = 6-18$ , we find for  $l_i$  values of about  $1.8 \cdot 10^{-6} \text{ cm}$  and for  $v_i$ ,  $1.0-2.0 \cdot 10^4 \text{ cm/sec}$ . This uncertainty in the values of  $l_i$  and  $v_i$  greatly impede comparison with experimental data in charge transfer theory in aerosols. We will note also that the mode of charge transfer to particles is determined in this case by the "Knudsen ion number"  $\text{Kn}_i$ , the value of which is several times less than the "molecular" number  $\text{Kn}$ , so that  $\text{Kn}_i = 0.13-0.18$  corresponds to the upper boundary of HDA particle radii which we have selected, namely  $10^{-5} \text{ cm}$ .

We will first examine the charging of particles by ions of the same sign in the absence of an external electrical field. The differential equation of stationary diffusion of ions to a particle in electrical field created by it has a form

$$\frac{4\pi D n_{\infty}}{E} \left( \frac{1}{\rho} - \frac{e^2 a^2}{2\rho^2(\rho^2 - a^2)} \right) \exp\left[\frac{\varphi(\rho)}{kT}\right] d\rho \quad (12.3)$$

where  $E$  is the voltage of the field. When  $Kn_1 \rightarrow 0$  we have the boundary conditions  $n = n_{\infty}$  for  $\rho \rightarrow \infty$  and  $n = 0$  for  $\rho = a$  and we arrive at the formula

$$\Phi_c = \frac{4\pi D n_{\infty}}{\int_a^{\infty} \frac{1}{\rho^2} \exp\left[\frac{\varphi(\rho)}{kT}\right] d\rho} \quad (12.4)$$

where

$$\varphi(\rho) = \frac{i e^2}{\rho} - \frac{e^2 a^2}{2\rho^2(\rho^2 - a^2)} \quad (12.5)$$

--the potential of electrical forces acting on an ion,  $e$  is the elemental charge;  $i$  is the number of elemental charges on a particle, positive for like ionic and particulate charges and negative for unlike. The first term in (12.5) corresponds to the Coulomb force and the second to mirror force. We assume here that the particle is a conductor of electricity, which is valid in most cases for extremely fine particles. It is assumed in the derivation of (12.4) that the process of diffusion of ions is quasistationary. Under what conditions this is true will be explained below.

To answer the question whether mirror forces can be disregarded in the theory of charging of HDA particles we will calculate their effect during diffusion of ions to an uncharged particle ( $i = 0$ ). The magnitude of the integral in (12.4) in this case is 0.97, 0.83 and 0.62 for  $a = 10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$  cm, respectively. Thus, mirror forces in HDA cannot be disregarded.

Proceeding to the case  $Kn_1 \rightarrow \infty$ , we will note that the mechanism of charging of particles by gaseous ions consists in the fact that ions in collision with particles give up their charge and fly off in the form of neutral molecules. Gentry and Brock [207] instead of disregarding mirror forces, make an incorrect assumption with Boltzmann distribution of ion concentrations around the particles. Since this distribution is governed by molecular collisions, and since the latter do not exist near a particle for  $Kn_1 \rightarrow \infty$ , the formula

$$\Phi_i = \pi a^2 \bar{v}_i n_{\infty} \exp(-i\epsilon^2/akT) \quad (12.6)$$

derived in the above-cited work is incorrect. Liu, Whitby and Yu [208] made the same mistake.

The correct solution of the problem is found in the works of Keefe, Nolen et al., [209-211], who solved the problem of the free trajectory of an ion travelling in an electrical field created by a particle. By disregarding mirror forces, these authors found for the ionic flux to a particle of opposite charge, in consideration of Maxwellian velocity distribution of the ions, the expression

$$\Phi_k = \pi a^2 \bar{v}_k n_{\infty} (1 - i\epsilon^2/akT), \quad (12.7)$$

which coincides with (12.6) only when  $i\epsilon^2/akT \ll 1$ . When mirror forces are taken into account the ionic flux to an uncharged particle is

$$\Phi_k = \pi a^2 \bar{v}_k n_{\infty} (1 + \sqrt{\pi\epsilon^2/2akT}). \quad (12.8)$$

In the case of charged particles the problem can be solved only by the mathematical method [211]. The values of the "electrostatic" factor  $\theta$  (inclosed in braces in (12.7) and (12.8)) are presented for this case in Figure 6 as functions of particle radius. The curves in this figure were plotted on the basis of the mean square velocities of the ions. As Keefe et al., show, the curves consider the velocity distribution of the ions and can be satisfactorily approximated by displacing the curves shown in the figure to the right so that the abscissas are 1.5 times greater. The authors assume in their calculations that ionic aggregates consist of eleven water molecules, i.e., they assumed  $m_i/m_g \approx 7$ .

The problem of the charging of particles at intermediate Knudsen numbers  $Kn_i$  is fraught with enormous difficulties and remains far from solved even today. Proceeding from formula (12.6), Gentry and Brock [207] found by the Knudsen iteration method an expression for  $\phi/\phi_k$  in a form with which we are already familiar. Lie, Whitby and Yu went even farther [208]: they assumed not only the Boltzmann distribution of ion concentrations near a particle, but also the Maxwellian (isotropic) distribution of their velocities and arrived at the conclusion that (12.6) is valid for all Knudsen numbers!

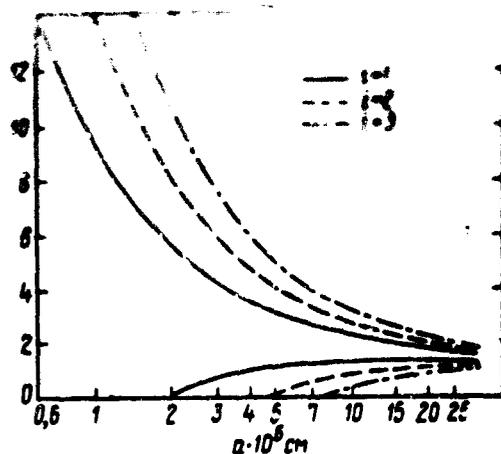


Figure 6. Electrostatic Factor During Diffusion of Ion to Charged Particle.

All other authors solved this problem by the boundary sphere method. The diffusive flux to it was determined on the basis of formula (12.4) in which  $a$  is substituted by the radius of the boundary sphere  $a + \beta L_i$ . The free molecular flux to a particle from the boundary sphere was calculated by various methods. Brickard [217] and Siksna [213] did not take into account the curvature of the trajectory of the ions in the electrical field of the particle. Keefe and coworkers [211] used in their calculations the results outlined above, which they obtained for  $Kn_i \rightarrow \infty$ , i.e., they assumed that the ions fly toward a particle as though from infinity. In his calculations Fuchs [214] assumed that the initial point of the trajectories of the ions lies on the boundary sphere. Natanson [215] selected as his boundary sphere, a sphere such that an ion experiencing a collision within it cannot be ejected from it. All above cited authors based their calculations on extremely varied values of  $L_i$  and  $\bar{v}_i$  and it is therefore difficult to compare their results. Since the boundary sphere method generally does not produce accurate results, it is hardly worthwhile to consider the question as to which of the above-mentioned methods is more accurate.

In all the foregoing we assumed the process of charging and discharging of particles to be quasi-stationary. Meanwhile, during each event of recharging of particles the distribution of ion concentrations around them must change. It is obvious that in order that the discharging process be considered quasi-stationary it is essential that the time of relaxation of the ionic atmosphere around the particles be much less than the average time that elapses between recharging events. As analysis of the problem indicates [214], the condition  $a^{3n_{\infty}} \ll 1$  when  $a \gg 10^{-5}$  cm must

be satisfied for this purpose. When  $a = 10^{-6}$  cm the more rigid condition  $a^2 n_0 \ll 0.01$  must be satisfied. In practice, these conditions may be regarded as satisfied, both in the laboratory and in the atmosphere.

Under the above stated conditions, as indicated by calculations, the electrical field created by the nonuniform distribution of ion concentration near a charged particle, i.e., the screening effect, may also be disregarded.

In the case where particles become charged in a bipolar-ionized environment, it can be assumed that ions of both charges diffuse toward the particle independently of each other. A stationary distribution, in which the number of particles with  $i$  charges of a given sign, which acquire yet another charge of the same sign per unit of time, is equal to the number of particles with  $i + 1$  charges, acquiring one charge of the opposite sign, will eventually be established in an aerosol, regardless of the initial distribution of the particles with respect to charges. For simplicity we will assume that an aerosol is monodispersed and that the concentration, mobility and other properties of ions of both signs coincide. By determining, on the basis of the above formulas, the fluxes of like and unlike ions to particles with  $i$  charges  $\phi_i$  and  $\phi'_i$ , we can formulate a series of equations

$$2\phi_0 N_0 = \phi'_1 N_1; \phi_1 N_1 = \phi'_2 N_2; \dots; \phi_i N_i = \phi'_{i+1} N_{i+1}, \quad (12.9)$$

when  $N_i$  is stationary concentration of particles with  $i$  charges, and hence we can find the distribution of particles in terms of charge (the coefficient 2 in the first equation is a result of the fact that an uncharged particle can capture an ion of either sign). We will note that this distribution is independent of ion concentration, although the rate of its establishment is proportional to  $n^\infty$ .

For large particles ( $a > 10^{-4}$ ), when formula (12.4) is applicable and mirror forces can be disregarded, this formula acquires one of the following forms:

$$\phi_0 = 4\pi D n_0; \phi_i = \frac{4\pi D n_0 e^i}{\exp \lambda_i - 1}; \phi'_i = \frac{4\pi D n_0 e^i}{1 - \exp(-\lambda_i)}, \quad (12.10)$$

where  $\lambda_i = |ie^2/akT|$ . It follows from (12.10) that  $\phi_i/\phi'_i = \exp(-\lambda_i)$ .

By multiplying equation (12.9) we obtain

$$N_i = N_0 \frac{\exp \lambda_i - 1}{\lambda_i} \exp \left( - \sum_1^i \lambda_k \right) = \quad (12.11)$$

$$= N_0 \exp (-i^2 \epsilon^2 / 2akT) [\exp (\lambda_i / 2) - \exp (-\lambda_i / 2)] / \lambda_i.$$

As shown by calculations the factor  $[\exp(\lambda_i/2) - \exp(-\lambda_i/2)]/\lambda_i$  for particles with  $a \geq 10^{-4}$  cm and with not very large charges (the overwhelming majority of particles fits this description) is quite close to 1. If we discard it we obtain

$$N_i = N_0 \exp (-i^2 \epsilon^2 / 2akT), \quad (12.12)$$

i.e., particle distribution with respect to charges is expressed by the Boltzmann equation.

We will note that formula (12.12) is extremely accurate when  $a \geq 10^{-4}$  cm, but as particle dimension decreases it becomes increasingly inaccurate. In connection with the method described in §4 for determining particle dimension according to the fraction of the charged particles in the stationary state, we point out that for  $a = 10^{-5}$  cm this fraction, calculated in accordance with the Boltzmann formula, is ~2% (relative) less than the more accurately calculated value, ~10% for  $3 \cdot 10^{-6}$  cm and about double that for  $10^{-6}$  cm.

Keefe et al., [212] used the Boltzmann particle distribution by charge a priori, and various explanations are given for departures from it for small  $a$ . Meanwhile, the Boltzmann equation is valid only for equilibrium states; if ions, having combined with particles, could break away from them in the form of ions, i.e., if there existed "detailed equilibrium", the Boltzmann formula unquestionably would be applicable. In reality, however, we don't have equilibrium here, but rather a stationary state.

As we already pointed out in the introduction, the number of elemental charges acquired by HDA particles in a bipolar ionic atmosphere is very small. By way of illustration we present a table, compiled by Fuchs [214], of HDA particle distribution by charge in the stationary state (rounded off to the nearest hundred).

TABLE 2. STATIONARY DISTRIBUTION OF HDA PARTICLES BY CHARGE IN BIPOLAR IONIZED ATMOSPHERE.

$\lambda$ (cm)	$10^{-7}$	$3 \cdot 10^{-7}$	$10^{-6}$	$3 \cdot 10^{-6}$	$10^{-5}$
Fraction of uncharged particles	0.99	0.95	0.76	0.51	0.29
Fraction of particles with 1 $\epsilon$	0.01	0.05	0.24	0.45	0.44
2 $\epsilon$	-	-	-	0.04	0.20
3 $\epsilon$	-	-	-	-	0.06
4 $\epsilon$	-	-	-	-	0.01

In the presence of an external electrical field the charge is superposed on the diffusion charge of the particles by the flux of ions moving in the field. In the case of unipolar ionization this flux is expressed by the Poten'ye formula

$$\Phi_E = 3\pi E n_{\infty} \beta a^2 (1 - i\epsilon/3Ea)^2, \quad (12.13)$$

where E is the field voltage. For comparison of this flux with diffusion flux we will examine the charge of a neutral particle with  $a = 10^{-5}$  cm. In this case we can express diffusion flux without large error by formula (12.10) for  $\Phi_0$ . This formula and formula (12.13) it is easy to find that

$$\Phi_E / \Phi_D = 0.75 \epsilon E a / kT = 0.9 \cdot 10^4 E a \quad (12.14)$$

or for  $a = 10^{-5}$  cm, expressing E in v/cm,

$$\Phi_E / \Phi_D = 3 \cdot 10^4 E. \quad (12.15)$$

This ratio is even smaller for particles of smaller dimension and for charged particles. Thus, the rate of "drift" charging of HDA is compared with the diffusion rate only in sufficiently strong fields (in excess of 3,000 v/cm), for instance, in electro-filters, and it can be disregarded in the atmosphere.

Proceeding to experimental data on the kinetics of the charging of aerosol particles by gas ions, we will point out that most of the measurements were made on comparatively large particles at atmospheric pressure, i.e., at small  $Kn_1$  numbers. Flanagan [216] measured the reduction of the stationary concentration of gas ions in air under the influence of the

polydispersed aerosol, formed by the heating of Nichrome with  $\bar{a}$  from 0.01 to 0.13  $\mu$ , i.e. for  $Kn_i > 1$ . Considering that the particles thereby did not acquire more than one elemental charge (which is true only for the lower end of this range), Flanagan was able from these measurements to determine the sum of values  $i_0$  and  $i_1$ , specifically  $i_0 + i_1 = 0.58 \bar{a}$ . For  $Kn_i > 1$  this dependence correlates thoroughly with the theory.

Liu, Whitney and Yu [216] measured the kinetics of the charging of monodispersed aerosols of dioctylphthalate with  $\bar{a} = 0.32$  and 0.67  $\mu$  by unipolar ions at pressures of 0.03 to 1 atm, i.e.,  $Kn_i \leq 1$  and found that the curve of particle charging as a function of time agrees satisfactorily with formula (12.6) which does not contain  $Kn_i$ , and the authors assumed this formula to be valid for all  $Kn_i$ . For this purpose, of course, they had to assume that the mass of the ions was 15 times greater than the mass of the neutral air molecules. As already pointed out, formula (12.6) is invalid at such  $Kn_i$  numbers, and it is impossible to explain how such agreement was achieved. Otherwise, it would have to be said that the charge tests conducted for low pressure cannot accurately simulate the process of charging of HDA particles due to the effect of mirror forces, the magnitude of which depends not on  $Kn_i$  but on particle dimension.

A number of researchers measured the ratio of charged and uncharged aerosol particles in the stationary state in a bipolar ionic atmosphere from which was calculated the relation

$$\Phi_1/\Phi_0 = 2N_1/N_0$$

These studies were made with polydispersed aerosols and can hardly be used for checking the theoretical calculations. Fortunately, in the tests of Pollak and Metniks [217] with aerosols obtained by the heating of Nichrome, for which  $\bar{a} = (1 - 4) \cdot 10^{-6}$  cm, it was found that the experimental values of the ratio  $N_1/N_0$ , in accordance with theory, are higher than those calculated according to the Boltzmann formula for  $\bar{a} < 1.35 \cdot 10^{-6}$  cm, but lower for larger particles. As pointed out by the above-cited authors, the reason for this is the polydispersion of the aerosols, and the larger the particles the more it distorts the results.

### 13. Thermophoresis and Diffusiophoresis in HDA

In our discussion of these complex phenomena we will confine ourselves only to the range  $Kn \geq 1$ .

A particle located in heterogeneous gaseous medium is acted upon by a force, known as thermophoretic if it is caused by the presence of a temperature gradient in the mixture, and diffusiophoretic in the case of a composition gradient. In these cases, as in the case of the problem concerning the resistance of a medium to particle motion, the force acting on area  $S$  of a particle is defined by the integral

$$F_{Tk} = - \int dS \sum_{\pm} \{ m_g |V_g V_g| f^{\pm} dV_g \}$$

where  $f^+$  and  $f^-$  are the distribution functions of gas molecules, the projections of whose velocities onto the direction of the concentration gradient are positive or negative, respectively,  $V_g$  is the velocity of gas molecules. The temperature gradient or concentration gradient appears in this equation in implicit form through the coordinate-dependent functions  $f^+$  and  $f^-$ . The causes of motion of aerosol particles under influence of temperature gradient differ for  $Kn \gg 1$  and  $Kn \ll 1$ . When  $Kn \gg 1$  this phenomenon is quite analogous to thermodiffusion. In the case of  $Kn \ll 1$  the cause of their motion is the existence of a temperature gradient within the particle itself and the tangential flow of gas along the unevenly heated surface of the particle.

In contrast to other transfer phenomena, even in the  $Kn \gg 1$  range, the zero approximation for  $f$  cannot be used in the calculation of thermophoretic force, since the gas is in a heterogeneous state.

The theory of gaseous thermodiffusion was used for solving the problem of thermophoresis in the free molecular regime by Einstein [219], Clusius [221], and in a more rigorous form, by Bakanov and Deryagin [223], and also by Waldmann, [222]. In the two latter works the Chapman-Enskog theory was used in the Lorentz problem, i.e., it was assumed that the mass of the aerosol particles is great compared to the mass of gas molecules and that the role of the collisions of molecules with each other is negligibly small compared to their collisions with the surface of particles. Assuming that part of the molecules  $1 - \phi$  is reflected in mirror fashion and the others are diffused, i.e., with Maxwellian distribution, corresponding to the temperature of the surface of a particle, the thermophoretic force will not depend on  $\phi$  and is expressed by the formula

$$F_{Tk} = - (32/15) (a^2/\mu_g) \nabla T \bar{v}_g, \quad (13.1)$$

where  $\Delta T$  is the temperature gradient,  $\chi_g$  is the thermal conductivity of the gas. In the case of a multi-atomic gas the value of the translation component of thermal conductivity,  $\chi_{gi} = 15\eta/4m_g$ , where  $\eta$  is viscosity, should be substituted into (12.1). Mason and Chapman [224] assumed that all molecules are reflected elastically, some of them in mirror fashion and portion  $\phi'$  in such a way as to retain absolute velocity, but in random direction. They obtained a value of  $F_{Tk} = 1 + 4\pi/9$  greater than according to (13.1). Mohchik, Inn and Mason [227], using a model of inelastic collisions developed by Wang Chang and Uhlenbeck [226], strictly substantiated the validity of formula (13.1) for multi-atomic gases.

The theory of thermophoresis in the range of intermediate Knudsen numbers was developed by Brock [227] by the Bkhatnagar method using Knudsen iteration. The thermophoretic force for a single component multi-atomic gas, according to Brock, is

$$F_T = F_{Tk} \exp \{1 - [0,06 + 0,09\alpha_m + 0,28(1 - \alpha_m)(\chi_a/2\chi_g)]Kn\}. \quad (13.2)$$

where  $F_{Tk}$  is given by equation (13.1),  $\chi_g$  and  $\chi_a$  are the thermal conductivity of gas and particle,  $\alpha_m$  is the coefficient of mechanical accommodation. This equation is equivalent to the empirical formula derived by Schmitt [228]

$$F_T = F_{Tk} \exp(-bKn), \quad (13.3)$$

assuming that for a monatomic gas

$$b = 0,06 + 0,37\alpha_m - 0,09\alpha_m(\chi_a/2\chi_g), \quad (13.4)$$

and for a multi-atomic gas

$$b = 0,06 + 0,37\alpha_m - 0,28\alpha_m(\chi_g^*/2\chi_g), \quad (13.5)$$

where  $\chi_g^*$  is the total thermal conductivity of a multi-atomic gas,  $\alpha_T$  is the coefficient of thermal accommodation.

The values of the constant  $b$  according to [229] are listed in Table 3.

TABLE 3. VALUES OF CONSTANT  $b$  IN EQUATION (13.3) FROM VARIOUS EXPERIMENTAL DATA.

Work	Aerosol Material	Gas	$b$	$\alpha_m$
[228]	Oil	Ar	0.39	0.8
[228]	Oil	N <sub>2</sub>	0.38	0.81
[228]	Oil	CO <sub>2</sub>	0.36	0.8
[228]	Oil	H <sub>2</sub>	0.22	0.79
[240]	Tricresylphosphate	Air	0.41	0.88
[241]	Amorphous NaCl	Ar	0.47	0.91
[234]	Crystalline NaCl	Air	0.46	0.91

Dwyer [230] recently developed the theory of thermophoresis in thirteen-moment approximation which, according to him, is valid for the entire range of Knudsen numbers. Such an assertion is unfounded, since a thirteen-moment approximation was developed for the slip-mode, i.e., for  $Kn < 1$ . The use of this approximation for describing coagulation kinetics [231] yielded results substantially different from the exact theory, even for  $Kn \approx 1$ . In the range  $Kn \rightarrow \infty$  Dwyer's result does not convert to the accurate formula (13.1), but predicts a monotonic diminution of  $F_{Tk}$  with increasing  $Kn$ . Dwyer's conclusion that  $F_T$  should have a negative value for values of the coefficient of mechanical accommodation  $0.9 < \alpha_c < 1.0$  contradicts all known experimental data [232].

Gardner [233] examined the problem of thermophoresis of an evaporating particle located in its own rarefied vapor in the absence of a carrier gas and proved that the thermophoretic force should be about the same in this case as in the absence of evaporation of the particle.

Experimental investigation of the thermophoresis of particles of silicone oil in Ar, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>, partially encompassing the range  $Kn > 1$ , was undertaken by Schmitt [228]. The tests were carried out through observation of the displacement of a single droplet in a Milliken condenser with plates thermostated at different temperatures. The particle radii varied from 0.7 to 1.2  $\mu$  and pressure was 10 to 760 mmHg so that the range of Knudsen numbers between 0.05 and 3.3 was encompassed. For  $Kn \approx 3.3$   $F_T$  is strictly proportional to  $a^2$ , which qualitatively proves the theory. In the range  $Kn > 0.2$  the experimental data are approximated by formula (13.5), and for all gases except H<sub>2</sub>,  $b = 0.38$ . For  $Kn \approx 3$  the

ratio of theoretical values of  $F_{TK}$  to experimental values in Ar, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> are 1.05, 1.21, 1.22 and 1.38, respectively, and experimental accuracy was lowest in the latter case. An analogous method was used by Schad and Cadz [234] for sodium chloride and mercury particles with particle radii of 0.22-1.15 and 0.096-0.145 , respectively, and here the range  $0.2 < Kn < 4.0$  was encompassed. Measurements showed  $F_T$  to be independent of the thermal conductivity of the particles, i.e., the measurements confirmed the conclusion of the theory, although the measured value was closer to the Haywood-Einstein theory than to the Deryagin-Waldman calculations.

Two partial cases should be singled out for examination of diffusio-phoresis--1) equimolecular counterdiffusion of two components and 2) diffusion of one component through a stagnant second component. The theory of diffusio-phoresis at large Knudsen numbers was developed by Waldman [235] and Deryagin and Yalamov [236]. In case 1 the force acting on a particle is:

$$F_{dk} = (8/3) a^2 n_g (2\pi kT)^{1/2} D_{12} (\nabla x_1)_\infty [m_{g2}^{1/2} (1 + \varphi_2 \pi/8) - m_{g1}^{1/2} (1 + \varphi_1 \pi/8)], \quad (13.6)$$

where  $D_{12}$  is the coefficient of mutual diffusion,  $x_1$  is the mol fraction of component 1,  $(\Delta x_1)_\infty$  is the concentration gradient of component 1 at infinity from the particle. For case 2:

$$F_{dk} = (8/3) a^2 n_g (2\pi m_{g1} kT)^{1/2} (1 + \varphi_1 \pi/8) D_{12} (\nabla x_1)_\infty / x_2. \quad (13.7)$$

Diffusive phoresis in the transition mode in a two-component mixture was investigated by Brock [237] using Bkhatnagar's model so as to limit the application of the theory to molecules with similar dimensions and mass. For case 1 and  $x_1 \gg x_2$ , assuming that  $\phi_1 = \phi_2 = 1$ :

$$F_d = F_{dk} \left\{ \frac{d_1^2 m_{g1}^{1/2} \cdot d_{12}^2 - 0.311 [2m_{g1} m_{g2} (m_{g1} + m_{g2})]^{1/2}}{(m_{g2}^{1/2} - m_{g1}^{1/2}) Kn} \right\}, \quad (13.8)$$

where  $d_1$  and  $d_2$  are the effective diameters of the molecules  $d_{12} = (d_1 + d_2)/2$ .

In case 2 and  $x_1 \ll x_2$ :

$$F_d = F_{dk} [1 - 0.071 (2m_2 / (m_2 + m_1))^{1/2} Kn^{-1}] \quad (13.9)$$

The values of  $F_{dk}$  in equations (13.8) and (13.9) are taken from (13.6) and (13.7), respectively.

Waldman and Schmitt [238] investigated diffusiophoresis for large and intermediate Knudsen numbers. They measured droplets of silicone oil at 20° for various binary gaseous mixtures. For case 1 they found agreement with formula (13.6) in the following mixtures:  $CO_2/C_3H_8$ ,  $N_2/C_2H_2$ ,  $N_2/C_2H_4$ ,  $N_2/C_2H_6$ ,  $N_2/O_2$ ,  $N_2/Ar$ . Brock [237] compared the theoretical values of the ratio  $v_d/D_{12}(\nabla x_1)_\infty$ , where  $v_d$  is the rate of displacement of the particle in the composition gradient field, for  $Kn \rightarrow \infty$  with the results of Waldman and Schmitt and found that there was agreement between nitrogen- $O_2$  mixtures and the above hydrocarbons. No agreement was found for  $N_2/Ar$  and  $CO_2/C_3H_8$  mixtures between the theory and experiment. This is explained by the great difference between the diameters of the components, which makes it impossible to use the simplified relaxation model of the kinetic equation of a binary mixture. For case 2 Brock found satisfactory correspondence for asymptotic values of the ratio  $v_d x_2 / D_{12}(\nabla x_1)$ , obtained from theory and experiment for  $Kn \rightarrow \infty$  in  $H_2O/N_2$  mixtures. By way of concluding our examination of thermal- and diffusiophoresis we might point out that the agreement between the corresponding theories in the transition range and the experiment is satisfactory. Nevertheless, it would be desirable to formulate a more general theory based on a strict approach to simulation of the collision terms in the kinetic equations of a binary mixture.

Brock [239] pointed out that there should exist yet another form of motion of aerosol particles, "photodiffusiophoresis", caused by a change in the physical or chemical equilibrium between particles and the gas atmosphere under the influence of electromagnetic radiation. For ordinary photophoresis, caused, as we know, by uneven heating of a particle by radiation, Brock proposed the term "photothermophoresis".

514. Coagulation of HDA

As Smolukhovskiy demonstrated, the problem of brown-in coagulation is mathematically equivalent to the problem of condensation of a vapor on a particle. Therefore, everything that was stated in §9 concerning mass transfer is also applicable to coagulation. The only difference is that the Knudsen number in the case of coagulation should be determined somewhat differently--primarily, the role of the mean free path of gas molecules here will be performed by the apparent (or effective, see p. 5) free path of aerosol particles, i.e., the average distance at which correlation with the initial direction of motion of the particle is lost. This distance is given by the relationship  $l_p = \bar{v}_p \tau$ , where  $\bar{v}_p = \sqrt{8kT/m_p}$  is the thermal velocity of the particle,  $\tau = m_p/B$ ,  $B$  is mobility,  $m_p$  is particle mass. Further, in the case of coagulation it is necessary to replace  $l_p$  with the corresponding value, which relates to the relative motion of two particles, i.e., by  $l_p \sqrt{2}$ . Finally, in place of particle radius it is necessary to substitute the radius of the absorbing medium  $r = 2a$ . In view of the above statement, the aerosol Knudsen number is expressed as  $Kn_p = l_p \sqrt{2}/2a$ . The values of  $l_p$  and  $Kn_p$  for spherical particles of unit density, suspended in air under normal conditions, are presented in Table 4.

TABLE 4. VALUES THAT CHARACTERIZE HDA COAGULATION.

Particle Radius, Å	10	20	50	100	200	500	1000
$l_p, \text{Å}$	659	468	300	220	164	124	113
$Kn_p$ number	46.4	16.5	42.4	1.56	0.58	0.176	0.08
Coagulation constant, K $10^{10}$ cm/sec:							
According to Smolukhovskiy	323	162	63.8	34.0	18.0	8.57	5.55
According to equation (14.1)	4.42	6.26	9.80	14.0	19.8	31.3	
According to Sakhni theory	4.39	6.14	9.67	12.0	11.0	7.1	5.14

At large Knudsen<sub>p</sub> numbers, obviously, the coagulation constant should be expressed by the formula for the number of collisions between gas

molecules, i.e., aerosol particles may be regarded as large gas molecules the probability of collisions among which is not influenced by the presence of another, light component (Lorentz gas):

$$K_p = 2\sqrt{2}\pi a^2 \bar{V}_p = 4(3a\bar{k}T/\rho)^{1/2}, \quad (14.1)$$

where  $\rho$  is particle density. The validity of this expression was proved rigorously by Hidy and Brock [242], who solved the kinetic equation for Lorentz's gas. The expression derived by them for the coagulation constant takes into account the electrostatic interaction among particles, influence of external fields and the presence of velocity gradients, but unfortunately does not include terms with molecular forces, which cannot but play some part in the coagulation of HDA, since their particle dimension is comparable to the background wavelength. The intermolecular interaction potential for two spherical particles of identical radius is described by the Gamaker equation:

$$U(R) = \frac{A}{6} \left[ \frac{2a^2}{R^3} + \frac{2a^2}{R^2} - 4a^2 + \ln \left( 1 + \frac{4a^2}{R^2} \right) \right], \quad (14.2)$$

where  $R$  is the intercentral distance;  $A = \pi q^2 \beta / 6$ ,  $q$  is the number of molecules per unit volume of the substance,  $\beta$  is London's constant. From the equation of moments it is easy to obtain the expression

$$b^2 = R_m^2 [1 - U(R_m)/E], \quad (14.3)$$

where  $b$  is sighting distance (see Figure 7),  $R_m$  is the minimum distance between particle centers,  $E$  is the total energy of the particle. Calculations by the successive approximation method indicates that the function  $b(R_m)$  in the range of values  $2a < R_m < \infty$  should have a unique minimum  $b_m$ . When  $b < b_m$ ,  $R_m$  becomes imaginary, i.e., the minimum distance of the trajectory from point 0 does not exist and the particles should collide. When  $b > b_m$ ,  $R_m$  has a real value and this corresponds to the case shown in Figure 6-- absence of collision. For two particles in motion  $E$  denotes kinetic energy of their relative motion for  $V = 0$ . The average  $E$  is therefore equal to  $3kT$ . In the absence of molecular forces  $b_m = 2a$ , i.e., the molecular forces are increased by a factor of  $b_m^2/4a^2$  the collision cross-section of particles and, consequently, coagulation constant.

By means of approximate calculation with the kinetic equation Brock [243] determined the coagulation constant for intermediate  $Kn_p$  numbers.

In his derivation each of the particles was regarded as a source of molecules with a perturbed distribution function. By colliding with the surface of another particle such molecules create a repelling force acting along the axis of the center. The formula derived by Brock is extremely complex. When  $Kn_p < 5$  the correction factor for free-molecular formula (14.1), which Brock derived, is the same as one, but as  $Kn_p$  is reduced to about two, this factor decreases somewhat and becomes a fraction of a percent less than one. However, at  $Kn_p \approx 2$  it begins to increase rapidly as  $Kn_p$  decreases. Thus, for  $Kn_p \approx .1$  the Brock formula predicts coagulation constants greater than the free-molecular values, i.e., produces a result that contradicts the physical concept upon which it is based.

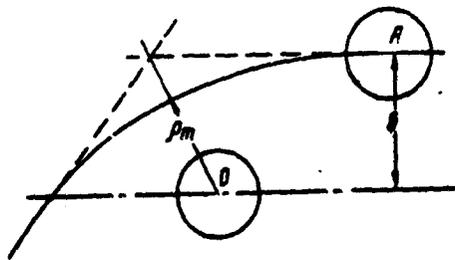


Figure 7. Trajectory of Particle in Central Field of Attraction.

Obviously, the method described in §9 using formulas (9.15) or (9.16) gives more accurate data concerning the coagulation constant. The coagulation constants calculated by this method are listed in Table 4. For comparison also included are values calculated according to equation (14.1) and also according to Smolukhovskiy's equation, the validity of which has already been checked by several researchers who are working on HDA.

Astakhov [231], for determination of the coagulation constant, used the so-called thirteen-moment approximation, but the formula which he derived gives correct values only in the range  $Kn_p < 1$ .

The question concerning the influence of molecular forces on coagulation at intermediate  $Kn_p$  numbers is extremely complex, since it is necessary to take into account the effect of lag of molecular forces at distances comparable to the background wavelength. Up to now no theoretical expression that takes into account molecular forces has been proposed for  $Kn_p \approx 1$ .

Noteworthy is the conclusion reached recently by Wang and Friedlander [244] to the effect that during coagulation of aerosols under conditions where the coagulation constant is a function of the Knudsen number, no self-perpetuating distribution of particles with respect to dimensions is established.

There has been very little experimental research concerning HDA coagulation. The chief difficulty in such studies are the substantial particle losses on the walls of the apparatus and connecting lines, caused by the high diffusion coefficient of the particles. Therefore, the classical method of studying coagulation--periodic determination of the concentration of particles in samples taken from the chamber--cannot be applied to HDA. It is not surprising that O'Conner [245] and Quon [246], who used this method, obtained inconclusive results from the point of view of theory, specifically, that the coagulation constant increases monotonically as particle dimension decreases in the range of intermediate  $Kn_p$  numbers, and even more rapidly than predicted by Smolukhovskiy's equation. O'Conner worked with room condensation nuclei, the composition and shape of whose particles could not be determined. Quon [246] used aerosols which are products of the incomplete combustion of hydrocarbons. Even though, due to the low count concentration, it was possible to assume that the aerosols consisted of individual particles rather than aggregates, the question of their shape and degree of polydispersion remained unanswered. Only qualitative information is available in [101] concerning the character of HDA coagulation.

Fuchs and Sutugin [98] used the flow method for investigating HDA coagulation. An aerosol with a high, a priori measured count concentration was passed in laminar flow through a wide tube and the ratio of the concentrations of HDA at the intake and outlet was measured nephelometrically. Before nephelometric analysis the HDA particles were enlarged to a dimension of  $\approx 0.5 \mu$  by means of condensation of dibutylphthalate vapors on them in a KUST apparatus [97]. In individual tests the diffusion losses

of the particles in the tube were determined, for which purpose a strongly diluted aerosol was passed through the tube. The initial count concentration was determined ultramicroscopically after dilution of the HDA in a specially designed diluter and after enlargement in the KUST instrument. The coagulation constants determined by this method for monodispersed NaCl aerosols with average particle radii of 25 and 45 Å were  $13.4 \cdot 10^{-10}$  and  $15.1 \cdot 10^{-10}$  cm<sup>3</sup>/sec. The measurement error was 11%. The magnitude of correction  $b_m^2/4a^2$  to the free-molecular expression for the rate of coagulation, governed by the influence of molecular forces, was also calculated. Using the London constant calculated by Mayer [247] from the absorption bands of NaCl in the ultraviolet range, a correction factor of 2.19 was obtained. In consideration of this correction the calculated coagulation constants were  $10.2 \cdot 10^{-10}$  cm<sup>3</sup>/sec for  $\bar{a} = 25$  Å and  $13.4 \cdot 10^{-10}$  cm<sup>3</sup>/sec for  $\bar{a} = 45$  Å. The latter of these values, at least, is in satisfactory agreement with the experimental data. The discrepancy between experiment and theory can be explained by some polydispersion of the aerosol and inaccuracy in the determination of the London constant.

The above-described procedure was used later [248] for measurement of the coagulation constant of monodispersed aerosols of dioctylsebacinate with  $\bar{a} = 100$  Å. The number  $Kn_p$  in these tests was 1.54. The experimental coagulation constant was  $13.4 \cdot 10^{-10}$  cm<sup>3</sup>/sec, i.e., somewhat higher than given in Table 4. In the given case the discrepancy is completely explained by experimental error and the influence of molecular forces.

Stockham [13] calculated the coagulation growth of silver particles and found that his experimental data can approximate the theoretical values if values 2-10 times greater than according to the free-molecular expression are used for the coagulation constant. The discrepancy between theory and experiment increased as the concentration of the vapor from which the aerosol was formed increased. This is obviously related to the formation of branched chain aggregates during coagulation of aerosols with a high weight concentration. At low concentrations, as follows from electron microscopic photographs made by Stockham, the aggregates were compact, and, under these conditions the coagulation constant was about two times greater than the free-molecular value, which is in good agreement with the factor of the influence of molecular forces on silver particle coagulation, equal to 2.21, calculated in [6].

From the above results it can be concluded that there is satisfactory agreement between theory and experiment in connection with the question of HDA coagulation.

The theory of coagulation of charged aerosols in the molecular and transition modes is mathematically equivalent to the theory of the charging of aerosol particles. In the free-molecular mode the coagulation

constant of charged aerosols can be calculated with the aid of an expression derived by Hidy and Brock [242]. For intermediate  $Kn_p$  the corresponding calculations were made only on the basis of the boundary sphere method [249].

#### 515. Capillary Effects and Structure of HDA Particles

In addition to the features inherent to HDA in relation to transfer phenomena, optical and electrical properties, there are features in their thermodynamic properties, most of important of which--high vapor pressure of fine particles--is expressed in the familiar Kelvin equation:

$$\ln(p/p_0) = -2M\sigma/\rho RTa \quad (15.1)$$

where  $p_0$  is equilibrium vapor pressure over a plane surface,  $p$  is the vapor pressure over a droplet of radius  $a$ ,  $\sigma$  is the surface tension,  $\rho$  is the density of the material. The Kelvin effect becomes notable starting with a droplet dimension of 0.1 to 0.3  $\mu$ , and increases rapidly as  $a$  decreases, which is one of the reasons for instability, and even impossibility of producing HDA from materials possessing a vapor pressure that is not too low at room temperature. Lamer and coworkers [95, 250] subjected relation (15.1) to indirect experimental checking on droplets of sulphuric acid and dibutylphthalate. Recently, direct observations were made of the rate of evaporation of liquid particles of Pb and Bi and of solid Au particles under the electron microscope on a carbon substrate [251]. These tests, in which particle dimensions were 100 to 500  $\text{\AA}$ , also verified the validity of the Kelvin equation.

Higher pressure over a surface of positive curvature is sometimes referred to as the capillary effect of the first kind. Dependence of surface tension on surface curvature and dependence of the pressure in a droplet and of its density on dimension are ascribed to capillary effects of the second kind.

Tolman [252] was the first to prove the existence of the dependence  $\sigma(a)$  is the logical outcome of Gibbs' thermodynamics. He derived the integral equation:

$$\ln(s) = \int_0^a \frac{(\partial \sigma / \partial a) [(\partial \rho / \partial a) - (\partial \rho / \partial a) - (\partial \rho / \partial a) - (\partial \rho / \partial a)]}{(\partial \sigma / \partial a) [(\partial \rho / \partial a) - (\partial \rho / \partial a) - (\partial \rho / \partial a) - (\partial \rho / \partial a)]} da. \quad (15.2)$$

where  $\delta_0$  is the magnitude of the interatomic distance. In the first approximation

$$\sigma_0 = \frac{1}{2} \delta_0 a. \quad (15.3)$$

Here  $\sigma_0$  is surface tension of a plane surface. The theory of surface tension of curved surfaces underwent further development [253, 254, 255], in which the inaccuracy of Tolman's conclusions, related to equalization of pressure in a droplet and in a macroscopic volume of liquid, is eliminated. In these works the pressure was calculated by means of various equations of state. For  $\delta_0$  the following integral equation was derived:

$$\int_{-\infty}^{+\infty} (R + \delta_0) |p_0 - p_{xx}(R)| dR = 0 \quad (15.4)$$

where  $R$  is the radial coordinate;  $p_{xx}$  is the tensor component of pressure describing the forces acting perpendicular to  $R$  on an element of spherical surface. The function  $\sigma(a)$  is of tremendous importance in the theory of spontaneous condensation, although, as pointed out by Kirkwood and Buff [256], it is not permissible to consider this function alone, ignoring the reduction of density of fine particles. Radial density distribution and surface tension of particles with diameters 3-25 times greater than the molecular dimension were calculated by Plesner [257] using the equation of state for solid spheres possessing an attraction potential inversely proportional to the sixth power of distance. The result reached in this work was astonishing--the surface tension of such droplets is independent of dimension and amounts to  $\sim(1/3) \sigma_0$ . This means that in some range of dimensions--rather narrow, since experimentally the function  $\sigma(a)$  does not hold true all the way up to values of curvature of  $10^{-6} \text{ cm}^{-1}$ ,--there should be a sharp reduction in the value of  $\sigma$ . The latter seems improbable. According to Plesner, macroscopic density is not reached in extremely fine particles, even at their center.

Shcherbakov [257, 258] stated that for extremely fine particles the excess free energy inherent to them is related to the entire volume of the droplet as a whole, and not simply to the surface. He also found that the simple statement of the function  $\sigma(a)$  in the Gibbs-Kelvin equation cannot lead to the correct result and that it is necessary to add to this equation a term that contains  $d\sigma/d\sigma$ . Gibbs and Kelvin previously expounded an analogous point of view, although their opinion was based only on

intuitive premises. Shcherbakov examines surface tension as the amount of excess free energy related to unit area of a particle. The function  $\sigma(a)$  according to Shcherbakov, has the form:

$$\sigma = \sigma_0 \left( 1 - \frac{2}{ka} + \frac{2}{k^2 a^2} \right), \quad (15.5)$$

where  $1/k \approx 2-5 \text{ \AA}$ . Due to the increasing influence of the third term on the reduction of a the function  $\sigma(a)$  has a minimum and at extremely small  $a$  increases as dimension decreases. This result is in disagreement with the results published in [252-255] and with a conclusion recently reached by Bellemans [260] in his generalization of the Mayer theory of the equation of state for the case of a system containing an interphase boundary of arbitrary curvature.

The Cahn-Hilliard theory [261, 262] and the Hart theory [263] of surface tension, based on the consideration that the density of free energy is a function of concentration and concentration gradient of molecules, also predict a monotonically increasing function  $\sigma(a)$ . According to this theory, at high supersaturations in dense vapors, the particles of the liquid phase have an extremely diffuse surface, and their density can differ only slightly from the density of the vapor. Developing this theory, Hart [264] arrived at an extremely important conclusion. The fact is that in Hibbs' theory of surface tension the value of  $\sigma$  is constant in relation to the choice of position of the interphase boundary in the transition region between the phases. For a curved surface, however, this invariance does not hold true and the calculated value of  $\sigma$  depends on the position of this boundary. In this case the position of the boundary and the value are found from the condition  $d\sigma/dR = 0$ , where  $R$  is the radial coordinate. Hart established that under certain conditions the function  $\sigma(R)$  may not have a minimum, i.e., the concept of surface tension becomes meaningless. Okuyama and Zung [187] analyzed theoretically the dependence of the evaporation coefficient on curvature; these authors stated that the existence of this dependence is the consequence of the need to take into consideration the effort expended in increasing the area of the droplet after the combining with it is one more molecule. Considering this circumstance they found that

$$\alpha_r = \alpha_{c0} \exp(-\epsilon_0/kT), \quad (15.6)$$

where  $\alpha_{c0}$  is the condensation coefficient on a plane surface,  $\epsilon_0$  is the energy of activation of adherence to the surface at  $0^\circ \text{ K}$ . In the opinion of these authors  $\epsilon_0$  is equal to the surface energy of the droplet, divided by the number of molecules  $n$  within it. Then

$$\alpha_c = \alpha_{c0} \exp(-4\pi a^2 \sigma / nkT). \quad (15.7)$$

Substantial reduction of  $\sigma$  [subscript illegible], calculated using  $\sigma_0$ , becomes notable, starting with  $a \leq 100 \text{ \AA}$ , and for water at  $0^\circ\text{C}$  and  $a \sim 1 \text{ \AA}$ ,  $\alpha_c$  decreases by a factor  $10^8$  in comparison with  $\alpha_{c0}$ . Obviously, consideration of the function  $\sigma(a)$  should greatly weaken, if not eliminate this effect.

Reduction of the melting point of fine particles is described by the Thompson formula:

$$\Delta T_m / T_m = 2\sigma v_l / La \quad (15.8)$$

where  $\Delta T_m$  is reduction of the melting point compared to the macroscopic value  $T_m$ ,  $v_l$  is the mol volume of the liquid,  $L$  is the heat of fusion. The capacity of HDA particles to remain for a long period of time in the amorphous state and their capacity to agglomerate or stick together on coming into contact are related to a reduction in the heat of fusion. The results of an entire series of studies [32, 36, 46] indicate that particles of condensed HDA are usually amorphous. This fact is in agreement with the Ostwald law of stages and is unique, considering that the free energy of formation from a vapor of the seed of the liquid phase is less than for the formation of crystalline seeds. The crystallization of aerosol sediments of aluminum [32] and the oxides of several metals [36] requires heating or x-ray irradiation. It was shown in [45] that NaCl particles measuring  $\sim 10^{-7}$  cm last for a long time in the amorphous state in dry air. In humid air, however, large particles recrystallize after a few hours and the fine particles immediately become crystals.

The capacity of highly dispersed particles to adhere or agglomerate on contact has an extremely strong effect on the character of their coagulation. As we know, the Tamman temperature, at which solid bodies begin to agglomerate, is equal in the absolute scale to 0.6, the melting point for many bodies [265]. The existence of the dependence of the Tamman temperature on particle dimension was proved theoretically by Higuchi [266].

A sharp reduction in the specific area of the sediment of nickel aerosol with a particle dimension of  $\sim 30 \text{ \AA}$  at room temperature after several hours was described in [38]. It is interesting to note that the influence of the composition of the atmosphere, in which the sediment was located, on this process could not be determined. Coagulation of silver aerosol with a particle dimension of  $100 \text{ \AA}$  is accompanied by agglutination and adherence of particles even at  $120-150^\circ$  [6], i.e., much below the normal Tamman temperature. Reduction of this temperature by several hundred degrees for the sediments of the HDA of a number of refractory materials was noted in [37]. It is precisely the capacity of particles to adhere during coagulation that limits the production of highly dispersed powders through the aerosol state [6].

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