General and Inorganic Chemistry

Strong effect of minor impurities in a gas on the rate of evaporation of solid surfaces

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Evaporation of surfaces of quartz, corundum, and germanium monoxide precipitates in a flow of nitrogen and air was studied by the method of molecular nuclei of condensation, which makes it possible to determine extremely low concentrations of molecules from 10^2 to 10^8 per 1 cm^3 of a gas. The appreciable effect of low concentrations of gas impurities on the rate of evaporation of solid surfaces was found and studied in the region of low evaporation rates. Equations describing the dissimilar effects of the retention of molecules of impurities on the surface on the rates of evaporation and reverse condensation were proposed.

Key words: molecular nuclei of condensation, evaporation of molecules from a solid surface, effect of impurities.

The method of molecular nuclei of condensation (MoNC) is based on the existence of highly supersaturated, but quite metastable systems in which the role of condensation nuclei initiating the phase transition can be played by single nonionized molecules, radicals, or atoms that are able to chemically add molecules of so-called developing agents in the gas phase.[1–4] These systems consist of a gas (air, nitrogen, argon, *etc.*) containing supersaturated vapors of developing agents. Low-volatility compounds with high molecular weights containing active functional groups (carboxyl, amino, or ester groups) and capable of reacting with the molecule acting as the nucleus of condensation are used as developing agents. For clusters consisting of molecules of the developing agent, collected by the nucleus of condensation, to markedly decrease the barrier to the formation of an aerosol particle, the critical seeds of the developing agent should consist of a very small number of molecules. Supersaturation of the vapor of the developing agent is created steadily in a continuous gas flow using special condensation amplifiers of the light scattering with fogs (CASF). The process of supersaturation in this setup is based on the mixing of flows having different temperatures. In some cases, the diffusion principle of supersaturation is also used.

The main scheme of the MoNC method includes[3] conversion of the molecules of an impurity into MoNC, condensation of the developing agent on the nuclei of the supersaturated vapor, and measurement of the concentration of the resulting particles of the monodisperse aerosol. The conversion of the molecules of the impurity to be determined into MoNC requires a physical or, sometimes, also a chemical treatment, capable of transforming these molecules into new molecules which, in

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turn, can add the molecules of the developing agent in the gas phase. The majority of organometallic compounds can undergo conversion into MoNC. The transformation of metal carbonyls occurs most readily; they are destroyed by ultraviolet irradiation or by thermal treatment, and the active radicals thus formed are oxidized with atmospheric oxygen. If the molecules of an impurity contain a heteroatom that can form a nonvolatile oxide, the products of their conversion act as MoNC. Since heteroatoms are present in organometallic compounds (OMC), the method of MoNC makes it possible to determine very low concentrations of these compounds (down to 10^{-14} mol. %). However, the MoNC method also allows detection of impurities of compounds that contain no heteroatoms but are capable of forming nuclei of condensation, such as halides, alcohols, simple hydrocarbons, and even hydrogen and water vapor, but in this case, the threshold of sensitivity is several orders of magnitude lower than that in the case of impurities of OMC.

It is of interest to find out in what manner the MoNC method behaves toward substances, whose molecules are not converted into molecular nuclei. It is possible that the role of the nuclei of condensation in the anomalies observed can be played by molecules evaporated from the walls of quartz tubes, when they are heated or irradiated during the thermally or photo induced conversion, rather than by the direct products of conversion of the molecules of substances to be detected. In this case, impurities that cannot be converted can alter the properties of the evaporated molecules or the rate of their evaporation. In the former case, the effect is homogeneous, while in the latter case, it is heterogeneous. The purpose of the present work is to experimentally verify the suggestions concerning the mechanism of the transformation of impurities in the MoNC method. Some cases of specific effect of impurities in their homogeneous contact with evaporated molecules, associated with variation of the activity of MoNC, have also been observed. These cases are not discussed here.

Experimental

The scheme of the experimental setup is shown in Fig. 1. Two symmetrical arms of a T-tube (*13*), made of quartz glass and equipped with identical electric heaters (*15*), differed in that one of them contained a section of a source (*14*) of condensation nuclei evaporating at a lower temperature than the other sections of the tubes. Both arms of the T-tube were preheated in a nitrogen flow at 850—900 °C for several hours with the heaters being gradually moved to the point of junction. This treatment was carried out to remove contaminants and the most volatile impurities. This was probably accompanied by a decrease in the energetic inhomogeneity of the surface. Consequently, the temperature threshold of the appearance of the condensation nuclei in a flow of a pure gas increased from 200 to 600 °C. After that either a layer of a more volatile compound, for example, germanium monoxide, was applied onto one of the arms of the T-tube near the junction or the inner surface of the tube was finished, in order to create new "nontreated" surface. In both cases, the contaminants introduced were removed by repeated brief heating.

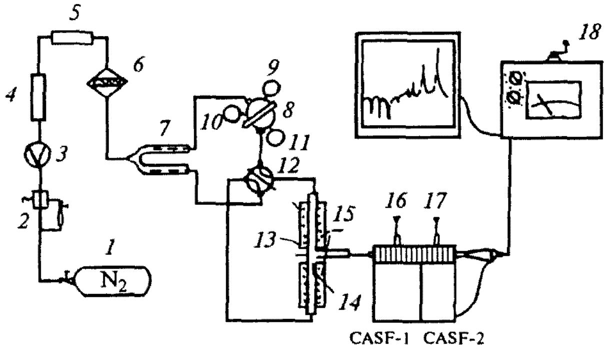

Fig. 1. Experimental setup for separate study of heterogeneous and homogeneous effect of admixtures: cylinder with N_2 (*1*), flow rate regulator (*2*), injector (*3*), activated charcoal (*4*), Pd catalyst (*5*), aerosol filter (*6*), T-tube (*7*), dosing apparatus (*8*), expendable sources of gas admixtures (*9—11*), cock (*12*), T-tube (*13*), source (*14*), electric heater (*15*), auxiliary flow for saturation with a developing agent (*16*), auxiliary flow for saturation with an "enlarger" (*17*), and aerosol photometer (*18*).

The velocity of the nitrogen flow from a cylinder, which could be varied using a flow rate regulator, was determined from the pressure difference on the injector. The carrier gas was purified from impurities by activated carbon, palladium catalyst, and an aerosol filter. The flow was divided in the T-tube by the capillaries into two equal portions. One of them was directly carried to the cock, and the other portion was passed through a dosing apparatus equipped with expendable sources of various gas admixtures *9—11*. This made it possible to direct admixtures of the vapors of various substances from the dosing apparatus either to the part of the nitrogen flow that passed through the arm of the T-tube containing the source, or to the part of the flow that bypassed the source. After that the flow moved successively to two CASF-1 and CASF-2 units for mixing flows with different temperatures, which led to the supersaturation of vapors of substances that develop and enlarge the condensation nuclei giving monodisperse aerosol particles. In most of the experiments, the developing CASF-1 unit was disconnected, since molecules evaporated from the surface of quartz glass acted as active nuclei, and the supersaturated vapor of diisobutyl phthalate in the CASF-2 unit sufficed for their transformation into aerosol particles. The variations of the aerosol concentration on brief (2 s) introduction of an admixture into one or another branch of the quartz T-tube were recorded using an aerosol photometer with an automatic recorder. The design of the dosing apparatus made it possible to inject admixtures at a constant gas flow rate.

Most of the experiments were carried out using tubes of quartz glass (S5-1, 10—1.3 mm in diameter) and corundum (or sapphire, 6—1 mm in diameter) and also with the precipitates of the condensate of the germanium monoxide vapor applied onto the inner surface of these tubes. The concentration of molecules evaporated from the heated surfaces into the flow of nitrogen (0.8—1.0 L $\min^{-1}$) was measured, and the effect of various gas admixtures on the intensity of evaporation was investigated.

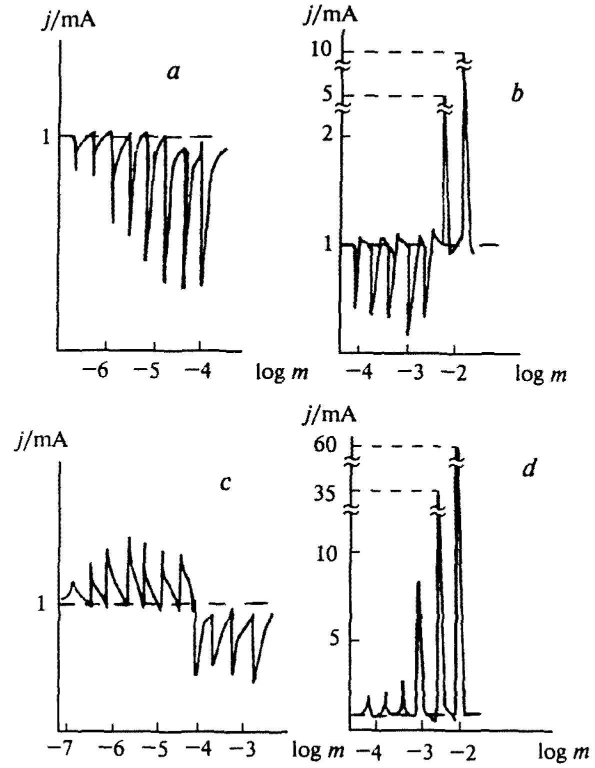

Fig. 2. Effect of an admixture of benzene vapor (log *m*) on the intensity of the recorder signal (*j*) reflecting the concentration of molecules evaporated from the walls of the quartz tube: tube after prolonged treatment (*a*), new tube (*b*), and tube after local heating with a gas burner (*c*), recorded at the section of the tube where the condensate previously appeared (*d*).

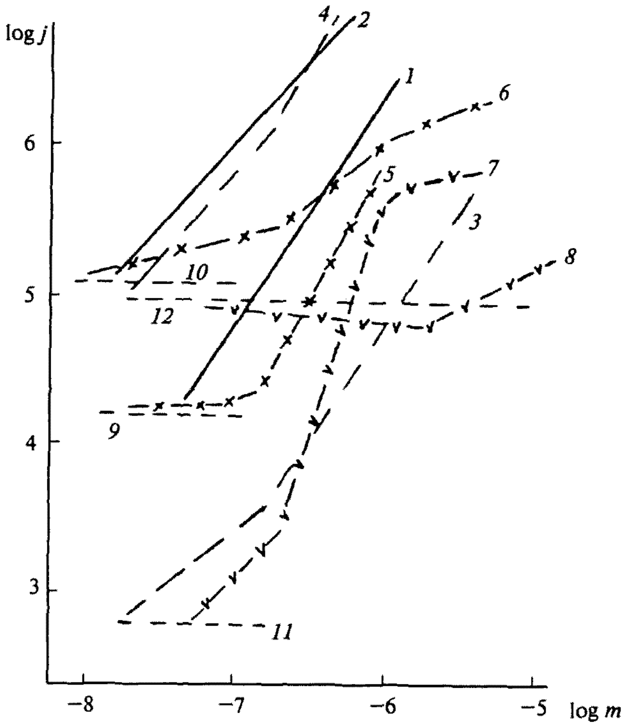

Fig. 3. Effects of admixtures of hexachloroethane and decane (log *m*) on the intensity of evaporation of the surface of the quartz tube (log *j*): effect of hexacloroethane after treatment without a flow at evaporation temperatures of 560 (*1*) and 760 °C (*2*) and in a flow at 560 (*3*) and 760 °C (*4*); effect of decane after treatment without a flow at evaporation temperatures of 560 (*5*) and 760 °C (*6*) and in a flow at 560 (*7*) and 760 °C (*8*). Level of the background of evaporated molecules after treatment without a flow: 560 (*9*) and 760 °C (*10*) and in a flow: 560 (*11*) and 760 °C (*12*).

To study the effect of admixtures on only the rate of evaporation of the quartz glass, we have simplified the thermal reactor. The new design included only a heater and one tube without a flow separator. This reactor was used to study the dependences of the magnitude and the sign of the signal of the photometer on the concentration of various impurities and on the temperature of the quartz tube surface being evaporated. The temperature was determined on the basis of measurements of the electric current in the circuit of the heater at a particular flow rate of nitrogen. The heater was preliminarily calibrated with respect to a thermocouple of Chromel cupel.

The measurements, the scheme of which is presented in Fig. 2, were carried out in the following way. At a certain steady-state mode of heating the tube, the level of the background, *i.e.*, the concentration of the aerosol particles grown by the MoNC method on the molecules evaporated from the surface of the tube in a pure gas flow prior to the injection of admixtures into it, was recorded. A known amount of a particular admixture was injected into the flow for a short period (~2 s) using a dosing apparatus. The injection of the admixture led to a variation of the concentration of the evaporated molecules, which was recorded using an aerosol photometer with an automatic recorder. Approximately 25 s later, the concentration of the evaporated molecules reached its maximum or minimum, and reached again the background level. The abscissa axis in Fig. 2 lays off the concentration of the admixture injected by the dosing apparatus, and the ordinate axis shows the intensity of the signal of the automatic recorder. Four series of measurements carried out after injection of benzene vapor are presented. In the first series, a new slightly treated tube was used; the tube used in the second series was subjected to a more prolonged treatment; the third series was carried out after local heating of the tube with a gas burner, and the fourth series of the experiments was conducted at the section of the tube located behind the heater, and some of the evaporated molecules condensed on its surface.

To study the effect of the properties of the surface on the rate of evaporation, two pretreatment procedures were chosen. The first procedure involves uniform heating of the tube for 4—5 h up to a temperature of 950—1000 °C in a stationary gas phase. In this version, all the evaporated molecules are condensed back to the surface. The material composition of the surface is thus retained. Only the surface microstructure can change due to the migration of the surface atoms. The second procedure suggests uniform heating in a gas flow that created a concentration gradient across and along the tube. The gas contained an admixture of an organohalogen compound that caused a dramatic increase in the concentration of the evaporated molecules in the gas flow. This version is directed at depletion of the surface of volatile components and at the points of the relief microstructure that are readily evaporated.

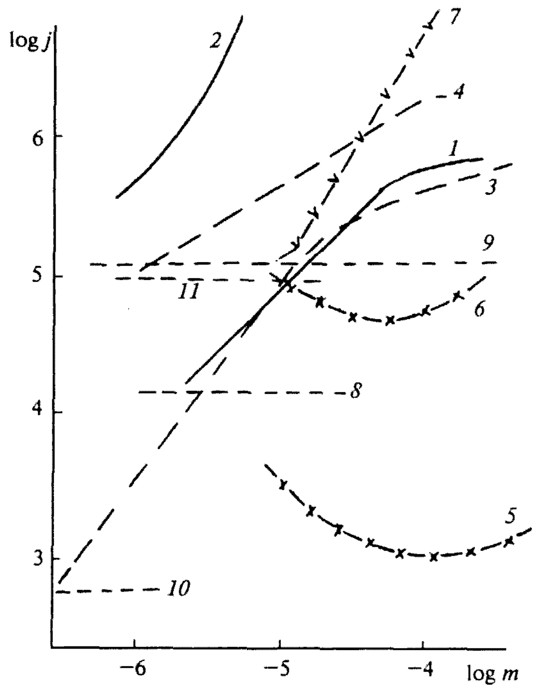

Fig. 4. Effect of admixtures of carbon tetrachloride and benzene (log *m*) on the intensity of evaporation of the surface of the quartz tube (log *j*): effect of carbon tetrachloride after treatment without a flow at evaporation temperatures of 560 (*1*) and 760 °C (*2*) and in a flow at 560 (*3*) and 760 °C (*4*); effect of benzene after treatment without a flow at evaporation temperatures of 560 (*5*) and 760 °C (*6*) and in a flow at 560 (*7*). Level of the background of evaporated molecules after treatment without a flow: 560 (*8*) and 760 °C (*9*) and in a flow: 560 (*10*) and 760 °C (*11*).

The results are presented in Figs. 3 and 4, but the dynamics of the signal advance is not shown there. During each measurement, the admixture was introduced continuously over a period of 15—30 s until a constant signal was achieved. The resulting values are represented by points in the curves of the dependence of the signal value on the concentration of the admixture. The abscissa axis lays off the logarithm of the molar fraction of the admixture and the ordinate axis lays off the logarithm of countable concentrations of the particles grown on the evaporated molecules. These measurements were carried out in an air flow, the purification system being the same as for nitrogen.

Results and Discussion

Analysis of the results presented in Figs. 3 and 4 indicates that the effect of impurities is very pronounced, since the concentrations of evaporated molecules change by 3—4 orders of magnitude. Along with the temperature of evaporation and the type of the impurity, the pretreatment of the surface being evaporated is also significant. The effects of admixtures of vapors of hydrocarbons and vapors of organic halides on the concentration plots are substantially dissimilar.

In the region of great concentrations of impurities reaching thousandths or hundredths of molar fractions, a dramatic jump of the signal has been observed in some cases. With an only 2- or 3-fold increase in the concentration, the signal increases by a factor of tens and sometimes by a factor of almost a thousand.

The method of MoNC makes it possible to measure the number of evaporated molecules in unit volume of the gas, *i.e.*, their overall concentration. It is determined from the concentration of aerosol particles grown on the molecules, which differs from the concentration of the molecules in the region of the end of the heated tube by the coefficient of losses and by the coefficient of development. The product of these coefficients under various experimental conditions varied from tenths to hundredths of fractions. At a measured concentration of 10 particles per cm^3 of the gas, the actual vapor concentration was 100—1000 molecules per cm^3 of the gas. Correspondingly, when the maximum concentration of particles was 10^6 per cm^3, the concentration of molecules was as high as 10^8 per cm^3. At higher concentrations, the role of coagulation increases. The whole range of concentrations that can be determined by the MoNC method is inaccessible for measurements by other known methods. The pressure of the quartz vapor was determined by traditional methods[5] in the temperature range from 1200 to 3200 K. The vapor pressures at lower temperatures were calculated from the heat of vaporization (564 kJ mol^{-1}) determined in the temperature range mentioned above. In the range of lower temperatures used, the components of impurities that are more volatile than quartz are evaporated from the quartz surface. When the surface is treated in a flow with an admixture that accelerates the evaporation, it becomes depleted of volatile components. The temperature dependence of the background increases. The heat of vaporization, calculated from the Clayperon—Clausius equation for the conditions of the treatment in a flow, is ~250 kJ mol^{-1}. This heat is more than two times lower than the heat of evaporation of quartz. When pretreatment is carried out under static conditions without a flow, all the components are retained, but the structure of the surface alters due to the recondensation of all the evaporated molecules. The temperature variation of the background after this treatment corresponds to a heat of evaporation of only 84 kJ mol^{-1}. The heat of evaporation in nontreated tubes has an intermediate value.

Since the temperature dependences of the vapor concentration over the surface of a solid at various versions of the pretreatment are different, one may assume that at low temperatures, the vapor exists in a nonequilibrium state. The nonequilibrium character of the low-temperature evaporation of a solid surface makes it possible to rationalize the effect of gas impurities on the rate of this process. This effect is due to the fact that the molecules of an impurity retain contact with the surface being evaporated and remain on it. This may be caused by a chemical reaction or by adsorption. Owing to the general character and the reversibility of the effect of impurities, the assumption of adsorption is more likely. Elevated temperatures necessary for evaporation are peculiar to activated adsorption. The particular mechanisms of the interaction may be different for various types of impurities and various surfaces. For example, the surface of microporous silica (Aerosil) is known to contain silanol groups, and special procedures of its treatment afford various chemical compounds.[6] It may be suggested that in some cases admixtures participate in the formation of chemical compounds. However, the effects found are reversible in the vast majority of cases, and, apparently, the mechanism by which the molecules of an admixture remain on the macroscopically smooth and heated (300—800 °C) surface of quartz glass involves adsorption processes.

Activated adsorption on nonuniform surfaces has been extensively studied in relation to problems of heterogeneous catalysis[7] and the chemical physics of a surface.[8] In particular, it was found that the nonuniformity of the surface is manifested in the fact that the characters of distribution of the heat and of the activation energy of adsorption are rather complex. To explain the effect of impurities, it is necessary to present the combination of all types of energetic microheterogeneities of the surface of solids and their interaction. The microheterogeneity of heats of evaporation is superimposed onto the pattern of energetic heterogeneity of the surface in the processes of activated adsorption. The nonsymmetrical blocking of the points of active evaporation and the regions of predominant condensation by the adsorbed molecules of the admixture may be considered to be the main reason for the observed effect of aqdmixtures on the rate of evaporation of a solid surface. The blocking of evaporation points decreases the concentration of the evaporated molecules in the near-wall layer of the gas, and blocking of the sites of condensation increases this concentration. The diffusion carryover of molecules to the gas flow and their measured concentration vary correspondingly. The degree and even the sign of the nonsymmetrical blocking depend on the temperature of the surface and on the concentration of the admixture. At low temperatures, there are only a few points of evaporation, and a low concentration of admixture suffices to block them. An increase in the concentration has a small influence on the amplitude of this effect, but increases its delay. As the temperature increases, the proportion of the surface occupied by the sites of the efficient condensation decreases, and the role of admixtures in the retardation of the condensation becomes more pronounced. When a certain threshold is attained, the surface of condensation becomes almost entirely blocked. In this range, the concentration of the evaporated molecules in the gas flow changes dramatically. The appreciable variability of the energetic nonuniformity of the surface allows deviations from the mechanism of blocking.

Along with the blocking of evaporation and condensation, strong interaction of the admixture with the surface, resulting in the displacement of weakly bound inclusions, is also possible. In this case, low-temperature intensification of evaporation will be observed.

Over a long period, the evaporation of nonionized molecules from the nonuniform solid surface, *i.e.*, purely thermal emission into the gas flow, could not be studied in the region of low evaporation rates, because there were no reliable methods for the measurements. The concentrations of evaporated molecules of solids, accessible for measurements by the MoNC method, are ~10 molecules per cm^3 of a gas. By using a counter of aerosol particles instead of an aerosol photometer, one can decrease the threshold of the measurements by three more orders of magnitude. This makes it possible to study the evaporation of solids at previously inaccessible low temperatures. The relative effect of the energetic inhomogeneity of the surface in this region is especially pronounced, since the $e^{\frac{\Delta E}{RT}}$ parameter, where ΔE is the difference between the heats of evaporation of the various regions on the surface, increases with a decrease in the evaporation temperature. When the rate of evaporation of the surface of a solid is low, the process is fairly stationary, due to the slow shift of the equilibrium, but the principle of detailed equilibrium is not obeyed. The activated adsorption of admixtures changes the ratio between the processes of evaporation and recondensation.

Under equilibrium conditions, the rate of evaporation of molecules from the surface of a tube into a stationary gas is equal to the rate of their recondensation. Using the accepted[9] designations, one may write

$$I_v a_v = I_c a_c, \tag{1}$$

$$I_c = n_0 \bar{V}/4, \tag{2}$$

$$n_0 = 4 I_v / a_c \bar{V}, \tag{3}$$

where $I_v a_v$ is the rate of the evaporation of molecules (cm^{-2} s^{-1}), I_c is the calculated frequency of impacts of vapor molecules on a surface (cm^{-2} s^{-1}) when their concentration is n_0 (cm^{-3}) and the average velocity of the heat motion is $\bar{V}$ (cm s^{-1}); a_c is the coefficient of condensation, equal to the ratio of the measured rate of condensation to the calculated frequency of impacts. The physical meaning of the evaporation coefficient a is not quite clear, but to achieve the full symmetry of the description of the direct and reverse processes, we formally assume that at a proper equilibrium $a_c = a_v$.

The gas flow changes the distribution of the concentration of the evaporated molecules across and along the tube. The varying concentration n (the average value over a cross-section) is equal to zero at the inlet of the heated area and gradually increases with an increase in the length l of the heated area. If l is sufficiently high, at the end of this area $n \to n_0$. The average concentration $\bar{n}_0$ in the stationary near-wall layer differs from n_0 only slightly, since the rate of the diffusion carryover of the evaporated molecules is low compared to the rate of the

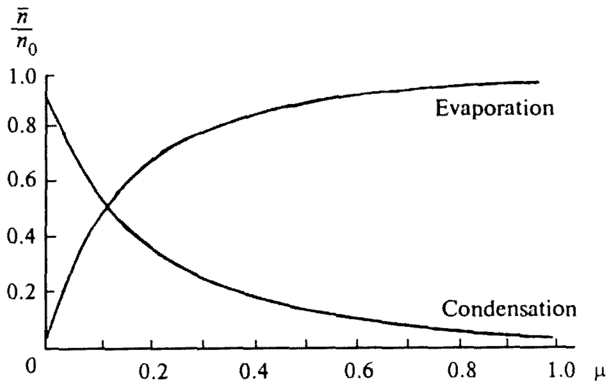

Fig. 5. Dependence of the ratio of the concentrations of molecules at the inlet to the concentration in a given point μ in a laminar gas flow, calculated from the equation $\bar{n}/n_0 = 1 - 0.82e^{-3.66\mu}$, on $\mu = Dl/vr^2$.

reverse condensation $I_c a_c$. Therefore, the balance equation for the flow can be written as follows:

$$2\pi rl(I_v a_v - a_c\bar{n}_0\bar{V}/4) = Vn \approx 0.9n_0, \tag{4}$$

where $2\pi rl$ is the surface of evaporation, V is the flow rate, and n is the concentration of molecules at the end of the heated area. To establish the relationship between n and n_0, one can use the known solution of the reverse problem, *viz.*, the problem of diffusion of particles from laminar flow to sorbing near the wall layer of a tube. Then n_0 is the concentration of particles at the inlet of the tube, and n is their concentration in the flow. The solution can be represented[10] as a power series of the dependence of n/n_0 on a dimensionless parameter:

$$\mu = Dl/vr^2 = \pi Dl/\bar{V},$$

where D is the coefficient of diffusion of particles in the gas, and v is the average linear velocity of the flow. This dependence is shown in Fig. 5. The reversibility of diffusion processes allows this dependence to be used for the calculation of the diffusion of molecules from the wall layer. One may assume that a diffusion flow of "holes," *i.e.*, sites not occupied by particles, moves strictly symmetrically to meet the diffusing particles. On this basis, we presume that the solution of our problem is adequately described by the complementary symmetrical curve in Fig. 5.

In most of our experiments, for the diffusion of the evaporated molecules, $\mu \approx 1.1$. As can be seen from Fig. 5, the value $n \approx 0.9n_0$ corresponds to this magnitude. If we substitute all the numerical values in expression (4) and ignore the difference between $\bar{n}_0$ and n, we obtain

$$n_0 = 2.9I_v a_v/(1 + 0.7a_c\bar{V}). \tag{5}$$

The effect of an admixture can be represented as a series of functions, $f_v(m_i)$ and $f_c(m_i)$, that show the degree to which the evaporation and condensation are blocked by the adsorbed molecules of an i-th admixture (from 0 to 1). With allowance for these functions Eq. (5) assumes the form

$$n_0 = \frac{2.91I_v a_v(1 - f_v(m_i))}{(1 + 0.7a_c\bar{V})(1 - f_c(m_i))}. \tag{6}$$

Complete blocking of the evaporation or the condensation ($f_v(m_i) = 1$ or $f_c(m_i) = 1$) is unlikely. According to Eq. (6) this can occur if either $n_0(m_i) = 1$ or $n_0(m_i) = \infty$. However, a substantial difference between $n_0(m_i)$ and n_0 is quite possible. Of special interest is the case where $f_v(m_i) \to 1$. Then $n_0(m_i) >> n_0$, which means high supersaturation of vapor under isothermal and isobaric conditions of evaporation from a surface in contact with an admixture with respect to a free surface. When evaporation is carried out in a flow, this should be observed at the end of the heated area at large μ values.

Actually, the experimental concentration of aerosol particles grown on evaporated molecules is $n_a \approx n_0$. The signal of the effect of admixtures shown in Figs. 3 and 4 is presented as the logarithm of the ratio between the photocurrents j of an aerosol photometer measured with and without the admixture. In our symbolism, this is the ratio of (6) to (5).

$$\frac{n_a(m_i)}{n_a} = \frac{1 - f_v(m_i)}{1 - f_c(m_i)} \tag{7}$$

$$\Delta \log j = \log\frac{1 - f_v(m_i)}{1 - f_c(m_i)} \tag{8}$$

The sign and amplitude of the effect of the admixture, in conformity with expression (8), depend only on the ratio between the effective regions of evaporation and condensation that have remained unblocked. If evaporation decelerates, the effect of the admixture is manifested as a negative signal, whereas in those cases where recondensation decelerates, the effect of the admixture yields a positive signal. The cases when the signal dramatically increases on a slight variation of the concentration are accounted for by the virtually complete blocking of the recondensation. In this case, the rate of evaporation approaches the rate of evaporation into a vacuum.

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