Reviews

Molecular nuclei of condensation. Conditions for observance and physicochemical features

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The formation of aerosol particles on molecular nuclei of condensation (MoNC) is considered. An interpretation of this phenomenon, consistent with the physicochemical features of MoNC and with the observed regularities, is proposed. The nucleation is induced by the addition of two or several vapor molecules of a developing agent to MoNC to give clusters that are more stable than spontaneous heterogeneous fluctuations. The physical properties of the supersaturated vapors of empirically selected developing agents conform to the condition of low concentrations of heterogeneous fluctuations, which is needed to observe MoNC.

Key words: aerosols, molecular nuclei of condensation, ultrasmall concentrations, clusters; nucleation; impurities, air tightness; highly sensitive chromatographic detector.

The formation of aerosol particles on individual active molecules of admixtures referred to as molecular nuclei of condensation (MoNC) was discovered by the author more than 30 years ago.[1] Based on this phenomenon, methods for determining impurities in a broad range of ultrasmall concentrations,[2] inaccessible using other known methods, have been developed.[3] Methods based on MoNC are used most efficiently to check highly leak-proof articles, for example, heat exchangers of fast-neutron nuclear power stations, fuel elements, Dewar vessels, *etc.*, and high-performance filters. These procedures require determination of large concentration drops of a test compound. The method of MoNC makes it possible to perform these measurements over a range of fourteen orders of magnitude and does not require any complex equipment or a vacuum. There are prospects for using an MoNC-based detector in chromatography. Other aspects of the investigation and application of MoNC have been discussed in numerous publications.[4—9]

In this work, we outline and interpret the main experimental findings characterizing the phenomenon of MoNC.

General information about the phenomenon of MoNC and methods based on it

The properties of MoNC are typical of molecules or atoms that have been evaporated from the surface of a solid into a gas stream at room temperature or molecules of volatile substances converted into new active molecules or radicals. The transformation (conversion) of molecules of volatile impurities into MoNC is carried out using physical (for example, UV irradiation or slow discharge[10]) or chemical (for example, reaction with ozone) treatment of these compounds in a gas (air, nitrogen, or argon) stream. Gas ions arising in these experiments either occasionally or as a result of various types of treatment are removed by applying an electric field.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 208—213, February, 1998.

The method of MoNC makes it possible to determine directly or indirectly almost any impurity in air or in an inert gas. The conditions for determination of many types of particular impurities have been described in detail in a previous publication;[7] therefore, now we restrict ourselves to a few typical examples. In an air stream, MoNC are formed most readily from admixed molecules of organometallic and organosilicon compounds; for this purpose, it is enough to expose a section of the stream flowing in a transparent quartz tube to UV light. The radicals generated upon photodissociation are oxidized by atmospheric oxygen. Active MoNC arise if this oxidation yields molecules of nonvolatile oxides, for example, Mn_2O_4 or SiO_2. However, a single $Fe(CO)_5$ molecule cannot be converted into Fe_2O_3 because it does not contain the second iron atom. It can be suggested that in this case an unusual molecule, FeO_2, is formed. Some impurities of another type are converted into MoNC on exposure to UV radiation without formation of radicals. Vaporized mercury atoms excited by the light of a mercury lamp are converted in air into MoNC in the form of HgO. These species are identified by treating them with ozone, which reduces HgO to the metal.[7] Excited SO_2 molecules are oxidized into SO_3, and in moist air they generate MoNC in the form of H_2SO_4.

The conversion of hydrocarbon molecules present as impurities requires a higher-energy treatment, for example, an electric discharge.[10]

The active radicals thus formed are able to act as MoNC during or after chemical interaction with reagents in the gas phase. The optimal combination of physical and chemical methods of treatment needed to convert admixture molecules into MoNC should be selected for each particular problem.

Indirect applications of the method of MoNC are based on the fact that the ability of MoNC to be developed is activated or deactivated upon interaction with impurities in the gas phase and also on the discovery that minor gas impurities can exert a considerable effect on the vaporization of a solid surface.[7,8]

Active MoNC combine with one another upon collisions, giving bimolecular or polymolecular species. This property accounts for the existence of an upper limit of the concentrations of MoNC: $n^{\cdot} \le 10^7$ cm^{-3}; in this case, the quantity of bimolecular species formed during the time of residence in the gas stream (no more than 1 s) does not exceed 1%. Before the conversion, volatile impurities can be present without any concentration limits. The lower limit of measurable concentrations of MoNC is governed by the range of determination of the concentrations of aerosol particles. Photometric instruments make it possible to determine concentrations of the order of 10 particles per cm^3; the limit of determination attained with particle counters is three orders of magnitude lower. Collisions between MoNC are impossible over the whole range of ultrasmall concentrations, 1 cm^{-3} < $n^{\cdot}$ < 10^7 cm^{-3}.

The concentration restrictions hamper the comparison of the methods of MoNC with other known methods. The $n^{\cdot} \ll 10^7$ cm^{-3} range of concentrations is inaccessible using other methods (with rare exceptions, one of which is the case of pure short-lived radioactive isotopes[3]), whereas in the $n^{\cdot} \gg 10^7$ cm^{-3} range, the regularities of MoNC methods are distorted. In a study dealing with this topic,[3] ^{211}Pb atoms with a half-life of 36 min resulting from the decay of ^{219}Rn atoms present in the gas phase were specially used for comparison with the MoNC method. In this case, Pb atoms act as molecular or atomic nuclei of condensation. A correlation between the number of Pb atoms and the formation of aerosol particles was observed; this confirmed that no more than one atom per particle was formed.

Substances, in whose supersaturated vapor the effect of MoNC is manifested are referred to as developing agents for MoNC. Compounds of this type, which have been selected experimentally, are characterized by fairly large molecular weights and low vapor pressures and contain reactive functional groups (carboxyl, amino, or ester groups) in their molecules.

It will be shown below that the molecular weight and low volatility are the main factors that ensure the necessary physical properties of the metastable supersaturated vapor of a developing agent (MSVD). Active groups in the molecules of developing agents are responsible for the interaction with MoNC *via* chemical or dispersion forces.

Supersaturated vapors are created using setups[7,9] in which a heated developing agent is evaporated and the vapor is cooled in a gas stream maintained at room temperature. These setups, together with other equiment used in the MoNC methods to determine ultrasmall concentrations of impurities in gases, have been described in a previous publication.[7] The scheme of this method implemented as calibration measurements is presented in Fig. 1. The observations are carried out in a steady-state gas stream. In experiments in which the concentration of the admixed molecules converted into MoNC can be dosed, the dependence of the gain in the concentration of aerosol particles (Δn_a) on the concentration (m) of the admixed molecules is measured. Examples of these dependences are presented in Fig. 2. In these examples, MoNC were obtained from molecules of metal carbonyl vapors by exposing them to UV radiation in a gas stream. For all carbonyls, the direct dependence $\Delta n_a = \chi m$ holds over a broad range of concentrations. The proportionality coefficients χ are substantially dissimilar for various carbonyls. The difference between the χ values is mostly due to the different probabilities χ_0 of the transformation of the MoNC into an aerosol particle, because the coefficients of conversion[4,7] of carbonyl molecules into MoNC differ only slightly. If the measurements are carried out with increasing degrees of supersaturation, small χ_0 values increase and approach unity. All the coefficients are leveled; however, in parallel with the increase in the concentration of

MoNC caused by their induced formation Δn_a, the concentration of MoNC resulting from their spontaneous formation, n_a, also increases. A typical example of the relationship between the three functions of supersaturation (Δn_a, n_a, and χ_0) is presented in Fig. 3. In a broad range of n_a, the Δn_a value increases proportionally to it and reaches a steady state when χ_0 approaches unity. This flattening-out means that all the MoNC have been converted into aerosol particles, while their spontaneous formation is still in progress. For the subsequent theoretical considerations, it is significant that the curve contains a section in which the $\Delta n_a/n_a$ ratio is constant. This clearly indicates that the kinetics of spontaneous and induced formation of aerosol particles are similar. In the region of very small Δn_a, n_a, and χ_0, in which $\Delta n_a/n_a$ increases with a decrease in the degree of supersaturation (decrease in n_a), this is due to the fact that the relative concentration n'_0 of the clusters based on MoNC increases at $\Delta n_a \to 0$.

The examples of dependences shown in Figs. 2 and 3 are typical of a wide variety of MoNC and developing reagents. The dependences of Δn_a on m similar to those shown in Fig. 2 indicate that the supersaturated vapors of developing agents are appreciably metastable. The increase in the rate of nucleation by factors of tens of thousands following the introduction of MoNC does not cause noticeable changes in the concentration of the monomer vapor molecules; the coefficient of development remains constant.

The use of these dependences for practical purposes makes it possible to measure ultrasmall concentrations of diverse compounds that cannot be determined by other known methods.

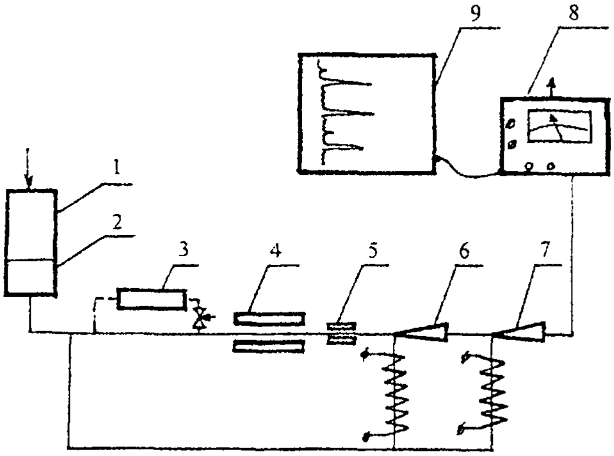

Fig. 1. Scheme for the sequential treatment of a gas stream containing an impurity to be determined. The method of MoNC in the modification of calibrating measurements: purification of the gas from aerosols (*1,2*); microdosing of the vapor of the impurity being analyzed (*3*); converting treatment (for example, UV irradiation) (*4*); removal of ions (*5*); dosing of heated vapors of the developing and enlarging agents (*6, 7*); measurement of the concentration of aerosol particles (*8*); recording of the measurements (*9*).

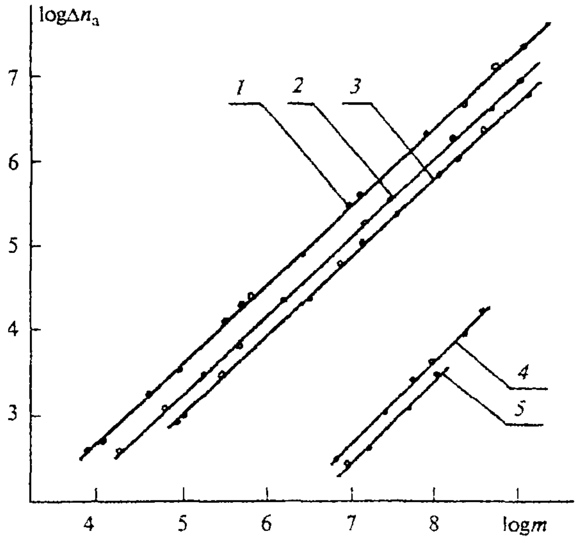

Fig. 2. Dependence of the gain in the aerosol concentration (Δn_a/cm^{-3}) on the concentration (m/cm^{-3}) of admixed carbonyl molecules in air: $Mn_2(CO)_{10}$ (*1*); $Ni(CO)_4$ (*2*); $Fe(CO)_5$ (*3*); $Cr(CO)_6$ (*4*); $W(CO)_6$ (*5*). Behenic acid was used as the developing agent. Diisobutyl phthalate was used as the enlarging agent (based on the measurements carried out by L. N. Pavlov and Ya. I. Kogan).

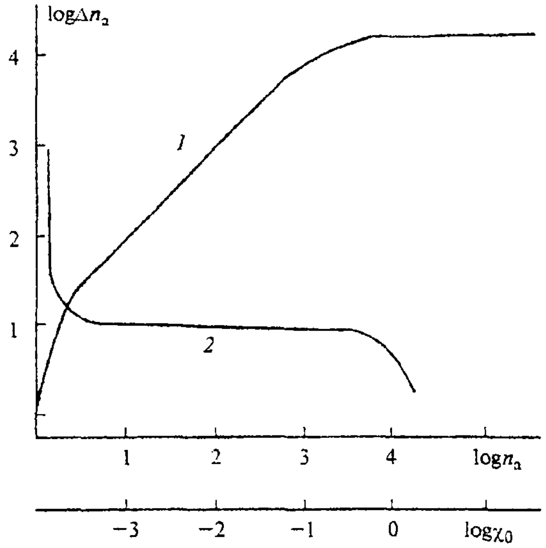

Fig. 3. Relationship between the concentrations of spontaneous (n_a/cm^{-3}) and induced (Δn_a/cm^{-3}) formation of aerosol particles (*1*) and their ratios (*2*) for varied degrees of supersaturation. The accompanying changes of the coefficient of development χ_0 (for a low-activity developing agent). Diisobutyl phthalate was used as the developing and enlarging agent (based on the measurements carried out by I. B. Vaganova and Ya. I. Kogan).

Physicochemical features of MoNC and the kinetic aspect of induced nucleation

Previous publications dealing with the phenomenon of MoNC have presented no satisfactory explanation of its physicochemical essence. Earlier[4] it was assumed (by analogy with specks of dust) that the number of vapor molecules of the developing agent g^0 collected and held by an MoNC should be close to the number of molecules in the critical embryo g^*. However, this estimate of g^0 is impracticably large. Unlike polymolecular species or ions, MoNC are characterized simultaneously by extremely small sizes and by short-range action of forces that fix the molecules of the vapor being condensed. This combination restricts the number of added molecules g^0 to the few closest neighbors. The spatial restrictions are additionally complicated by the fact that the vaporized molecules of a developing agent are normally much larger than the MoNC, and their interaction is additionally limited by the fact that a certain orientation of the molecules during the contact is needed. Therefore, for example, $g^0 = 6$ can be regarded apparently as a rare favorable case. For small MoNC, the $2 \le g^0 \le 4$ range should be considered to be more likely. The short-range forces binding the molecules of the developing agent to the nuclei of the clusters formed exert only a weak, if any, effect on the second layer of molecules, which is needed to attain the size of the critical embryo consisting of g^* molecules. If g^* is several times larger than g^0, the properties of critical embryos formed spontaneously in MSVD and the embryos containing clusters with MoNC are identical or nearly identical. Therefore, the stimulating influence of MoNC on the formation of aerosols is due to some specific features of MoNC rather than to a decrease in the required degree of supersaturation, as is the case with ions or particles of dust. The clear-cut difference between clusters formed by MoNC from g^0 molecules of the developing agent and similar spontaneous heterogeneous fluctuations is that the clusters are more stable, *i.e.*, the probability of their evaporation is lower. The stability of the MoNC-containing clusters results in the their appearance being independent of the statistically equilibrium concentration of heterogeneous fluctuations.

The concept of equilibrium distribution of heterogeneous fluctuations in an unsaturated vapor was introduced by Frenkel'.[12] As the first approximation, this distribution can be expressed in the following form:

$$n_g = n_1 \exp[-w_g/(kT)], \qquad (1)$$

where n_g is the concentration of heterogeneous fluctuations from g molecules of the condensed phase, n_1 is the concentration of vapor molecules, w_g is the work of formation of heterogeneous fluctuations of g molecules, k is the Boltzmann constant, and T is the temperature. In an unsaturated vapor, n_g monotonically decreases approaching zero as g increases.

Metastable systems containing supersaturated vapor of a developing agent are characterized by a similar quasi-equilibrium distribution of heterogeneous fluctuations (pre-embryos) for the region in which $n_g \le n_{g*}$. In this case, the concentration of critical embryos n_{g*} is a finite, although small, value. This approach is justified in the case where the concentration n_1 of the monomer vapor molecules changes only slightly upon nucleation. The real process of development of MoNC satisfies this condition (see Fig. 2).

Upon the introduction of MoNC, the distribution of concentrations of the pre-embryos based on MoNC-containing clusters adds to the distribution of concentrations of the spontaneous pre-embryos. The spontaneous pre-embryos are generated and evaporated instantaneously; their concentration is determined by the frequency of appearance and by the lifetime. The probability for a single fluctuation to grow to the critical size is very low. However, for a time-averaged concentration of the spontaneous pre-embryos n_g, a small fraction of critical embryos n_{g*} does exist. The relative distribution of the pre-embryos n'_g grown on the MoNC-containing clusters is similar to the distribution of n_g in the region in which $n'_{g0} \le n'_g \le n'_{g*}$. The stable population n'_g labeled by the clusters increases the overall concentration of the growing embryos, and the rate of nucleation thus increases. Correspondingly, the concentration of the aerosol particles formed during the existence of the supersaturated vapor of the developing agent in the gas stream also increases. The increase in the rate of nucleation, *i.e.*, the kinetic factor, accounts for the stimulating role of the MoNC.

A kinetic consideration* of a quasi-equilibrium system of particles consisting of 1, 2, ..., g, g^* molecules of a condensed substance assuming that the condensation and evaporation occur *via* addition and abstraction of a single molecule leads to the following expression for the concentration of particles consisting of g molecules:

$$n_g = K_{1g} n_1^g, \qquad (2)$$

where n_1^g is the monomer concentration to the power g, and K_{1g} is the equilibrium constant for the interconversion of monomers and g-mers.

A similar approach applied to the case where the system additionally contains MoNC, which results in the formation of non-evaporating g^0-mers, affords the following relation for the concentration of the g-mers ($g > g^0$) labeled by the molecular nuclei of condensation:

$$n' = K_{g0g} n_1^{(g-g^0)} n'_{g0}, \qquad (3)$$

where n'_{g0} is the equilibrium concentration of the g^0-mers labeled by the molecular nuclei of condensation, K_{g0g} is the equilibrium constant for the interconversion of labeled g-mers and labeled g^0-mers. Since the expressions for the concentrations of all the labeled

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* Proposed by B. Ya. Kogan.

g-mers include the first power of the $n^{\cdot}_{g0}$ value, this value is proportional to the concentration of MoNC. Equation (3) is also valid for the concentration of critical embryos:

$$n^{\cdot}_{g^*} = K_{g0g^*} n_1{}^{(g^*-g0)} n^{\cdot}_{g0}. \qquad (4)$$

It follows from expression (4) that a valid signal proportional to the nucleation rate in the method of MoNC should be proportional to the first power of the MoNC concentration.

If the properties of labeled and nonlabeled critical embryos are virtually identical and the g^* values for both of them are nearly equal, expressions (2) and (3) imply that the ratio of the valid signal to the background signal of spontaneous nucleation in the MoNC method is equal to

$$n^{\cdot}_{g^*}/n_{g^*} = (K_{g0g^*}/K_{1g^*}) n^{\cdot}_{g0}/n_1{}^{g0}. \qquad (5)$$

It follows from expression (5) that the $\Delta n_a/n_a$ ratio is also directly proportional to the first power of the MoNC concentration and is inversely proportional to the monomer concentration to the g^0 power; this, in principle, permits experimental determination of the g^0 values.

The above conclusion is of considerable interest; however, a comparison with experimental data requires special measurements of the concentrations of molecules in the MSVD at various degrees of supersaturation.

Physical properties of metastable supersaturated vapors of developing agents for MoNC

The first step of the stimulating action of MoNC is the formation of clusters consisting of an active molecule and two or several molecules of the developing agent. The addition of molecules of various impurities to some active molecules is a natural and frequently encountered process. At the next stage that involves the development of the clusters containing MoNC in the MSVD, some restrictions on the observance and measurement of these processes based on the stimulating influence of MoNC appear. The physical properties of MSVD needed to make the stimulating action of MoNC observable are ensured only by a limited range of substances. This is due to the fact that the range of concentrations of spontaneous heterogeneous fluctuations n_g in supersaturated vapors of various substances can be very broad. For example, in water vapors, at a degree of supersaturation $S = 4.2$ (S is the ratio of the real vapor pressure to the saturated vapor pressure), which is sufficient for the development of ions, the concentration of fluctuations consisting of six molecules has been estimated[13,14] as $n_6 \approx 10^{10}$ cm^{-3}. The maximum concentration of MoNC, $n^{\cdot} = 10^7$ cm^{-3}, is three orders of magnitude lower than the concentration of spontaneous fluctuations in a supersaturated water vapor. Other volatile liquids (for example, methanol or ethanol) used in Wilson cloud chambers[15] to observe ions are unsuitable for the development of MoNC for the same reason. The physical properties of MSVD, optimal for the development of MoNC, should satisfy the condition $n_g \approx n^{\cdot}_{\min}$, where $2 \le g \le 4$, and $n^{\cdot}_{\min}$ is the minimum concentration of MoNC in the range subjected to the measurements. Developing agents suitable for the observance of MoNC have been selected empirically. The compliance of the selected substances to the required physical properties of MSVD can be checked theoretically using formula (1). To calculate the work done to form a heterogeneous fluctuation w_g consisting of g molecules, it is necessary to use the drop model, which leads to large errors for embryos of small sizes. Nevertheless, these calculations make sense, because the size of particles consisting of two molecules of a developing agent and having large molecular weights is comparable with that of clusters consisting of tens of water molecules. For the calculations, we represent w_g in the following form:

$$w_g = A\sigma(g \cdot V_b)^{2/3} + g(\varphi_b - \varphi_a). \qquad (6)$$

where A is a coefficient that depends on the packing density of molecules in the pre-embryo and varies from 4.85 for dense spherical packing to $g^{2/3} \cdot 4.85$ for the most loose packing of spherical molecules; σ/erg cm^{-2} is the work spent for the formation of unit surface; V_b/cm^3 is the volume occupied by one molecule of the developing agent in the condensed phase ($V_b = M/\rho \cdot 6 \cdot 10^{23}$, where M/g is the molar mass, and ρ/g cm^{-3} is the density); φ_a and φ_b are the thermodynamic potentials of the MSVD molecules, in the condensed and gas phases, respectively. The data needed for the calculations have been obtained previously[14] for dioctyl sebacinate used as the developing agent. For the calculations in terms of Eqs. (1) and (6), the following parameters were accepted: $n_1 = 10^{12}$ cm^{-3} (for a degree of supersaturation $S = 3200$); $M = 426$ g; $\sigma = 31$ erg cm^{-2}; and $A = 4.85$. The numerical result was $n_2 = 10^{-1}$ cm^{-3}. The range of estimates of n_g for water and dioctyl sebacinate was so broad that conceivable errors of the calculations do not alter the general conclusion that an appropriately chosen developing agent makes it possible to obtain sufficiently low concentrations of the spontaneous heterogeneous fluctuations in the MSVD; these concentrations can be so low that a noticeable relative change in the rate of nucleation can be attained with one MoNC-containing cluster per 1 cm^3 of the gas. The decrease in the absolute rate of nucleation at low n_1 is counterbalanced by using fairly large degrees of supersaturations in MSVD.

All of the developing agents for MoNC selected empirically are characterized by low vapor pressures and relatively great molecular weights, which is in agreement with the small n_g required according to Eqs. (1) and (6). The same result could be attained, in principle, by using substances with large σ. The range of variation of σ for organic liquids is rather narrow, whereas the $\sigma = 465$

value of metallic mercury is too large. Attempts to obtain a condensation aerosol of mercury at room temperature failed.

We considered the physical properties of MSVD as the main factor determining the possibility of observing small concentrations of MoNC. However, the chemical properties of the molecules of developing agents are also significant. The efficiency of developing agents depends on the presence of chemically reactive groups able to interact with MoNC. This interaction determines the g^0 value for the MoNC-containing clusters and their stability. The coefficients of development for various MoNC in various developing agents differ by several orders of magnitude, the conditions for spontaneous nucleation being the same. The characteristic features of the chemical interactions involved in the phenomenon of MoNC and the specific chemical features of separate molecules present in ultrasmall concentrations will be considered elsewhere.[6]

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Received December 6, 1996;
in revised form October 21, 1997