MOLECULAR NUCLEI OF CONDENSATION

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Abstract

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Ya. I. KOGAN

MOLECULAR NUCLEI OF CONDENSATION

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1. The possibility was sought of initiating the growth of embryos of a dispersed phase in a metastable supersaturated vapor of some substance A by the action of individual, nonionized molecules of another substance B. The nontrivial character of the process sought is strengthened by the additional condition: $M_b < M_a$, i.e., that the mass of the molecular nucleus of condensation should be less than the mass of a molecule of the condensing vapor. Known electrically neutral condensation nuclei always consist of many molecules and always have substantially larger dimensions and mass than the condensing molecules. Molecular condensation nuclei, if they exist, must possess many other distinctive features: chemical specificity, thermodynamic stability (in the sense of the possibility of high equilibrium concentrations), a sharp lower-size boundary, a characteristic structure, and other properties of individual molecules. The present state of the theory of the problem does not make it possible to predict or deny with certainty the existence of molecular condensation nuclei with the properties proposed above. Meanwhile, establishing the fact of the existence and the conditions of manifestation of such nuclei is not only of theoretical interest, but may also have important practical consequences in the field of experimental technique at the molecular level.

2. A positive result of the search was obtained in a system consisting of an inert gas (air, nitrogen, or argon) with supersaturated vapor of dioctyl sebacate (DOS) as substance A, and with an admixture of molecules of dilute vapor of iron nonacarbonyl (DKZh) as substance B. The investigation was carried out in a continuous gas flow. Likewise continuous were the generation of molecular nuclei, the formation of supersaturated DOS vapor, the formation and growth of DOS embryos, and also all measurements of the mobilities of the nuclei and of the concentration of the grown embryos. The course of the processes in time was determined from the distribution of their stationary states in space along the direction of motion of the flow. The condensation nuclei were obtained by photochemical action on a strongly diluted admixture of iron pentacarbonyl (PKZh) vapor in a stream of pure dried air or nitrogen. The stream was passed through a tube of transparent quartz with a water jacket, which was illuminated by two PRK-2 mercury lamps placed in a cylindrical reflector coaxial with the quartz tube. The residence time of the mixture in the illuminated zone of the tube was about 1 sec.

It was assumed that the formation of DKZh molecules (condensation nuclei) proceeds by the reaction:

$$Fe(CO)_5 + Fe(CO)_5^* = Fe_2(CO)_9 + CO, \quad (1)$$

where the asterisk denotes an excited PKZh molecule ([1]). In additional experiments the nuclei were obtained directly by dilution of equilibrium DKZh vapor, and also from vapor of iron tetracarbonyl and from vapor of sulfuric acid. Besides air and nitrogen, argon with an oxygen content of less than 0.005% was used in these experiments. For metering the vapor admixture···

PKZh over a broad concentration interval, a 5-stage dilutor was used, which made it possible to regulate the dilution of saturated PKZh vapor within the concentration range from 10^{18} to 10^6 molecules $\cdot$ cm^{-3}. The minimum concentration of DKZh molecules was of the order of $10^3 \cdot$ cm^{-3}.

Supersaturation of DOS vapor was produced with the aid of the KUST-4 instrument—an improved version of the KUST-2 instrument described earlier ([2]). In both instruments supersaturation is produced by turbulent mixing of two gas streams: 1) a small stream heated before mixing and saturated, at the heating temperature, with vapor of the substance used, and 2) a large stream of colder gas containing the condensation nuclei under study. In contrast to the KUST-2 instrument, the KUST-4 instrument permits wide regulation of the thermostating temperature both in the evaporating and in the mixing parts of the instrument. In the present work, as a rule, the two instruments were connected in series: the primary condensation nuclei were developed in the KUST-4 instrument, which generated supersaturated DOS vapor; further growth of the growing DOS embryos to sizes convenient for counting aerosol particles occurred in the KUST-2 instrument through condensation of supersaturated diisobutyl phthalate vapor. Each growing DOS embryo was converted in the KUST-2 instrument into a stable aerosol particle of diisobutyl phthalate with radius $0.25 \pm 0.02\,\mu$. Measurements of the number concentration of the developing nuclei were made using universal visual-photoelectric nephelometer-ultramicroscopes based on the FEN-90 and FEN-58 instruments. The first was used as a nephelometer, the second as an ultramicroscope. Before entering the system, all gas streams were thoroughly purified of molecular and dispersed impurities by means of activated charcoal (preliminarily outgassed in vacuum at high temperature) and highly efficient anti-aerosol filters. Silica gel was used for drying; its layer reduced the relative humidity approximately to 1%. Ions from radioactive contamination and cosmic radiation were removed by an electric field in and in front of the mixer of the KUST-4 instrument. Under these conditions the background of spontaneously growing embryos was practically absent.

Fig. 1. Dependence of the concentration of nuclei on the concentration of PKZh molecules

3. The dependence of the concentration n (cm^{-3}) of developing nuclei on the

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concentration m (cm^{-3}) of PKZh vapor molecules was investigated. The results of these measurements are shown in Fig. 1. Curve In corresponds to full illumination of the photoreactor by two PRK-2 lamps; curve IIn was obtained when the lamps were screened by shutters admitting to the reactor an insignificant portion of scattered light. On both curves, for the region $n < 10^7$, a quadratic dependence $n \sim m^2$ holds over the general interval of m from 10^8 to 10^{12} cm^{-3}.* This result agrees with the assumption that nuclei are formed according to reaction (1), if the role of nuclei is played by single DKZh molecules. Pra-

* The deviation from the quadratic dependence in the region $m < 10^8$ on curve In is associated with the influence of traces of photochemically active impurities that sensitize additional formation of nuclei from PKZh; in the region $n > 10^7$, corresponding to the total concentration of nuclei formed in the photoreactor $n_0 = n/\eta\chi \approx 100n > 10^9$, it is associated with the influence of coagulation. The coefficient $\eta \approx 0.14$, accounting for loss of nuclei in the communications, and the coefficient of developability of nuclei $\chi \approx 0.07$ were determined by special experiments.

The correctness of this conclusion is confirmed by comparing the concentrations n_0 (Fig. 1) of nuclei formed in the photoreactor with the calculated number of collisions between PKZh and PKZh* molecules during their residence time in the photoreactor (1 sec). If the mean gas-kinetic diameter of the colliding molecules is taken as $\sigma_{1,2} = 0.5(\sigma_{\text{PKZh}} + \sigma_{\text{PKZh}^*}) \approx 1 \cdot 10^{-7}$ cm, then the calculation agrees with the data of the curve In_0 on the condition that approximately every thirtieth of all binary collisions between PKZh molecules takes place with the participation of PKZh* and leads to the formation of a condensation nucleus. An analogous comparison with the number of triple collisions of PKZh molecules leads to an absurdity—the number of such collisions is smaller than the number of nuclei formed. Additional evidence that the observed condensation nuclei are the direct result of photoreaction (1), without subsequent coagulation, is the decrease in the measured values of n when a buffer vessel is inserted between the photoreactor and the KUST-4 instrument.

4. Valuable information on the nature of our molecular nuclei is provided by measuring their mobility, characterized by the diffusion coefficient D. The usual method of measuring the mobilities of condensation nuclei by means of diffusion batteries, when applied to molecular nuclei, requires substantial corrections. The accommodation coefficient for such nuclei and the Fuchs coefficient may differ appreciably, respectively, from unity and from infinity, depending on the properties of the surfaces of the battery

channels. Special experiments showed that, in copper and glass tubes, an appreciable fraction of our nuclei is not captured upon collision with the surface. Therefore the measurement of D for molecular nuclei was carried out by us according to their ability to penetrate through a layer of granulated activated carbon. The calculation was made by the formula: $D = \bar{v}(\ln n_2 - \ln n_1)/Al$, where $\bar{v}$ is the mean linear flow velocity in the cross section of the layer, n_1/n_2 is the fraction of nuclei that have passed through the layer, l is the length of the layer, and A is a constant depending only on the aerodynamic structure of the layer. The constant A was determined in advance from vapors with known D and from larger condensation nuclei, for which comparison with a diffusion battery is legitimate. Both methods give good agreement of the results.

Further experiments showed that the value of D for molecular nuclei decreases noticeably when the air is insufficiently purified from impurities. With special additional purification of the air stream immediately before the photoreactor by a layer of activated carbon, previously degassed at a temperature of about 500° K, the measurements show an increase in the D of the nuclei. The maximum values of D for nuclei, measured in a clean stream at low concentrations of nuclei, proved to lie within the range 0.045–0.048 cm^2/sec. The calculated values of D for DKZh molecules are 0.046 cm^2/sec, and for Fe_2O_3, 0.1 cm^2/sec. Comparison of these results shows that in our case the condensation nuclei were precisely individual, free DKZh molecules, and not the product of their oxidation—Fe_2O_3 molecules. The latter, evidently, are formed only after aggregation of DKZh molecules into complexes of two or several molecules, which occurs only at the high initial concentrations of PKZh used in the photochemical production of iron oxide aerosols.

5. Molecular nuclei must possess an important distinctive property—thermodynamic stability in the gas phase at high counting concentrations. It is of great interest to verify the presence of this property by investigating, as a source of condensation nuclei, DKZh vapor in equilibrium with a solid macro-surface of crystals of this substance. In these experiments a small stream of pure gas (air, nitrogen, argon) was passed through a blackened glass tube filled with a layer of glass rings, on the surfaces of which a layer of DKZh crystals had been deposited. The gas saturated with DKZh vapor, immediately after the capillary outlet from the tube, was diluted with the main stream of pure gas and directed—

was introduced into the KUST-4 instrument under the usual operating conditions of the apparatus. To exclude the possibility of supersaturation of the vapor, the tube was thermostated at temperatures below room temperature. The experiments confirmed both the very fact of the "detectability" of molecules of unsaturated DKG vapor and the linear dependence of the concentration of detectable nuclei on the degree of dilution of the equilibrium DKG vapor (in contrast to the quadratic dependence for PKG molecules).

6. Thus, the fact that the growth of embryos of the condensed phase in

metastable supersaturated DOS vapor is initiated by individual nonionized DKG molecules has been established by three independent methods: from the kinetics of photochemical formation of nuclei, from measurements of their mobility, and from the "detectability" of molecules of unsaturated DKG vapor. By the last method, under analogous conditions, the detectability of molecules of other substances was found, in particular sulfuric acid and iron tetracarbonyl.* The effectiveness of searches for new systems and new conditions for the detection of molecular nuclei depends substantially on the correctness of the theoretical interpretation of the new phenomenon, in particular on an understanding of the mechanism of action of molecular condensation nuclei. A number of considerations and the results of certain specially designed experiments, a detailed report on which will follow, compel one to suppose that molecular nuclei are not necessarily centers from which embryo formation begins. Their initiating action is apparently associated with the acceleration of certain rate-limiting stages in the growth process of pre-embryonic complexes of condensing molecules. A foreign molecule adsorbed by such a complex catalyzes the attachment of free molecules, accelerating the formation of critical embryos.

The author warmly thanks all the colleagues who took direct part in carrying out the experiments and in developing the methods and instruments used in this work.

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CITED LITERATURE

[1] N. A. Belozerskii, *Metal Carbonyls*, Moscow, 1958. [2] Ya. I. Kogan, Z. A. Burnasheva, ZhFKh, **34**, 12, 2630 (1960).

* At present, about ten substances with molecular detectability of diluted vapor have been found in the laboratory.

Note: Figure translations are in progress. See original paper for figures.