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KINETICS OF DIFFUSION-LIMITED NUCLEATION IN A DIFFUSION CLOUD CHAMBER

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KEYWORDS

In the existing theories of homogeneous nucleation it is accustomed to consider that a concentration of a noncondensible (carrier) gas does not affect the rate of nucleation. Moreover, it is supposed that the higher the gas concentration, the closer the nucleation process is to the isothermal one for which classical nucleation theory (CNT) was originally built. However, in paper (Bertelsmann et al., 1996) and many others on the basis of the experimental data on homogeneous condensation of H_2O, D_2O and some alcohols in an inert gaseous atmosphere it was discovered that the critical supersaturation linearly increases with the increase of the carrier gas pressure P_0. Besides, with the temperature decrease a slope of isotherms $S_*(P_0)$ becomes more abrupt.

That is why the aim of this work was to consider in more detail the kinetic processes in DCC using some ideas specific for the kinetics of chemical reactions. In particular, as pointed out in (Frank-Kamenetskii, 1947) when a certain chemical reaction realizes in nature its observed rate is determined on the one hand by a real chemical kinetics on the surface of the interacting particles, but on the other hand by the rate of transport of the reacting medium to this surface due to the molecular or convective (in particular, turbulent) diffusion. As can be shown the second way becomes extremely important when the concentration of the reacting component is small (a rarefied vapor) as compared with the concentration of a carrier gas and simultaneously the rate of a chemical reaction is much more than the rate of diffusion.

Here we propose a model of the nucleation process under conditions when a transport of condensing molecules to the cluster surface is determined by their diffusion through a carrier gas. The main physical idea exploited within our approach is the following. If a certain cluster transits to another sort by attaching a monomer the rate of this process in the usual nucleation theory is proportional to a free-molecular flux of monomers on the surface of this cluster and this flux is determined by the volume concentration of monomers. Under the conditions of DCC this assumption stops to be valid because the real concentration of monomers at the external boundary of the Knudsen layer over the cluster surface differs from the concentration n_1 determined far from the cluster in view of the presence of a carrier gas. It is caused by the existence of a concentration jump in the vicinity of the cluster surface and the value of this jump becomes considerable when the mean free path of the condensing molecules in the carrier gas is of order of the cluster radius.

Further we use a special mathematical formalism which is strongly based on the microscopic theory of nucleation (Itkin and Kolesnichenko, 1997) put forward by the author and allows one to obtain an analytical representation of the cluster's concentrations through

supersaturation, the gas temperature and, that is quite new, the carrier gas pressure. It is shown that the usual conditions of experiments in diffusion cloud chambers where the concentration of the vapor is small, meet the requirements of the model validity that means this model can be adopted to explain a mechanism of the carrier gas pressure influence on the nucleation kinetics (Itkin, 1998) observed in experiments (Bertelsmann et al., 1996). In particular, as follows from our analysis instead of a usual supersaturation S all expressions of the theory contain a product $S\Theta$ where $\Theta \propto 1/P_0$ and depends upon the cross-section of the carrier gas and condensing molecules.

The main conclusion which can be made based on the above results is that at certain values of the temperature and, that is more important, pressure of a carrier gas a special regime of nucleation may establish. As follows from the presented analysis this case is realized at high pressures of the carrier gas, a large effective diameter (or cross-section) of the condensing molecules, comparatively low temperatures. We call this regime "diffusion-limited nucleation", but such processes are well known and even rather wide occur in chemical kinetics (Frank-Kamenetskii, 1947). However, for nucleation this effect here is considered for the first time.

From the results obtained it follows that in addition at the diffusion-limited nucleation the quasisteady concentrations of clusters as well as the rate of the evolution of the monomer's mass fraction α_1 become no longer be a function of two parameters — T and S, but three because now in addition they depend on the carrier gas pressure as well as on the nature of both the carrier gas and the condensing vapor. This dependence appears through the values of the collision cross-section and the mean free path of the vapor molecules through the carrier gas, and it must be taken into account when treating and comparing the experimental results with the others and with a theoretical prediction.

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