A MULTIMOLECULAR CONDENSATION MODEL AND AN ANALYTICAL METHOD FOR ITS SOLUTION

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As has been established in [1, 2], in a number of cases use of classical and quasichemical condensation models leads to disagreement with experiment. Thus, the data of molecular beam studies [3], obtained at moderate temperatures and pressures, indicate that clusters of large dimensions exert a major effect on the evolution of monomers, while analytical and numerical solutions of equations for the Szillard model performed in [2] indicate that dimers and trimers play such a role.

An attempt was made in [4] to explain this disagreement by the fact that the Szillard model does not consider nonequilibrium of the distribution of internal degrees of freedom within clusters. That study considered kinetic equations describing the evolution populations $x_j(k)$ of clusters of j molecules with internal energy $E_j(K)$. On the basis of the generalized quasisteady state method developed therein closed equations for cluster concentration were obtained in the limits of high and low pressure. It proved to be the case that only for a Boltzmann distribution of monomers over oscillatory and rotational degrees of freedom in the high pressure limit corresponding to large complexes ($j > r$, r being the parameter of the theory of [4]), do these equations coincide with those used in the Szillard model. However, in the low pressure limit (small complexes $j \leq r$) the equations differ significantly. The system of equations obtained in [4] will be termed the "multimolecular condensation model" below. An analytical method will be developed for solution of these equations, based on a nonlinear replacement of variables which is a generalization of the replacement used in [2].

Analysis of solutions has shown that at normal pressure and temperature small clusters do not affect the evolution of monomers. These results are in part similar to the conclusions of classical liquid drop nucleation theory [1]. At high pressure and temperature, on the other hand, the evolution of monomers is completely determined by their interaction with small clusters. The analytical solutions obtained for the multimolecular condensation model show that in contrast to the quasichemical model, upon consideration of nonequilibrium effects several condensation regimes may develop, controlled by the ratio of the parameters r, $j_* = 27j_{*cl}/8$ and the classical critical size criterion $j_{*,cl}$. The existence of such regimes permits description of a number of experimentally observed effects, not well described by existing models: In particular, anomolously high supercooling of water vapor in the high pressure region [5], the effect of uncondensed gas on the nucleation rate [6, 7], and the bimodal nature of the cluster distribution function over size observed in some experiments [8].

The physical meaning of increase in maximum supercooling ΔT with increase in pressure p (or temperature at the dew point) can be explained as follows. As is evident from the analytical solution, a discontinuity in condensation occurs at the point where the condition $j_* = r$ is satisfied. With increase in pressure the parameter r decreases, since clusters of ever smaller dimensions will correspond to the high pressure limit. The quantity j_* depends on T and p, and at the Wilson point (point of maximum supercooling), only on p. By differentiating the condition $j_* = r$ at the Wilson point with respect to p with consideration of the fact that $\partial r/\partial p < 0$, we find that $\partial \Delta T/\partial p > 0$.

Corresponding to the bimodality of the cluster size distribution function, a maximum appears in theory at $j_{*,cl} < r$. This maximum cannot be identified with similar extrema observed in numerical solution of the Szillard model equations [9], since this extremum is located at the point $j = r$ (r depends weakly on time), while the maximum described in [9] departs rapidly to infinity over the course of time.

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