Heteromolecular nucleation theory for multicomponent gas mixtures

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(Manuscript received 10 May, 1973)

This note reviews the heteromolecular nucleation theories which are given in greater detail elsewhere (Kiang et al., 1973*a*, *b*, *c*; Stauffer et al., 1973) together with the possible application of heteromolecular nucleation theory for the sulfur and the nitrogen cycle. This nucleation process involves multi-component mixtures of gases condensing together into small liquid droplets out of the gas phase.

To avoid misunderstandings we list here various notations: "Gas-to-particle conversion" is a name for all phase transition processes by which gases are transformed into the liquid or solid state. One step in this gas-to-particle conversion process is "nucleation" which can occur as "homomolecular" or "heteromolecular" nucleation depending on whether only one gas or at least two different gases simultaneously come together to form a liquid or solid phase. Both homo- and heteromolecular nucleation can occur as "homogeneous" nucleation (without a preexisting solid or liquid phase) or "heterogeneous" nucleation on already existing solid or liquid phases. Examples: Nucleation of pure water without impurities—"homomolecular homogeneous"; nucleation of water vapor on NaCl crystals—"homomolecular heterogeneous"; nucleation of sulfuric acid gas and water gas without further impurities or surfaces—"heteromolecular homogeneous"; nucleation of H_2O–H_2SO_4 gas on atmospheric aerosols—"heteromolecular heterogeneous". In general, nucleation is followed by the growth of just nucleated particles to larger sizes, either by homomolecular condensation or by heteromolecular condensation (incorporation of at least two different gases instead of only one sort of molecules).

For binary gas mixtures, the homogeneous heteromolecular nucleation theory, as developed by Flood (1934), Doyle (1961) and others, assumes a simple expression for the free energy ΔG of a droplet containing n_A molecules of type A and n_B molecules of type B:

$$\Delta G = -n_A kT \cdot \ln(P_A/P_{A_\infty} - n_B kT \cdot \ln(P_B/P_{B_\infty}) + (\text{Surface area}) \cdot (\text{Surface tension})$$

where P_A, P_B are the actual gas partial pressures and P_{A_∞}, P_{B_∞} are those of a vapor in equilibrium with a liquid mixture; P_{A_∞}, P_{B_∞} depend on the droplet composition n_A/n_B. P_{A_∞} and P_{B_∞} of liquid mixtures can be much smaller than the vapor pressures over the pure liquids A and B due to the mixing entropy; this vapor pressure reduction can be enhanced further by $A-B$-interaction. This vapor pressure reduction diminishes the gas pressure necessary for heteromolecular nucleation compared with the pressure needed for homomolecular nucleation. (This effects may be important for "homogeneous" nucleation experiments with unavoidable impurities, for example water impurities in ammonia.) For the H_2O–C_2H_5OH system, heteromolecular homogeneous nucleation theory and experiment agree well (Flood, 1934). For H_2O–H_2SO_4, already at 50 % relative humidity, droplets can grow to "infinite" size (Doyle, 1961) contrary to (homogeneous or heterogeneous) homomolecular nucleation of water alone.

Kiang et al. (1973*b*) give the heteromolecular homogeneous nucleation rate for H_2O–H_2SO_4 at 25°C and for H_2O–HNO_3 at 20°C, showing a strong dependence on the relative humidity. (We also give there the heterogeneous heteromolecular nucleation properties of ions in the usual model.) The gaseous H_2SO_4 concentration necessary for homogeneous heteromolecular nucleation may be reached in urban air; thus we think that H_2O–H_2SO_4 heteromolecular nucleation dominates the initial particle formation for the sulfur cycle. The problem of the nitrogen

cycle is less clear. The NHO_3 concentration calculated as the nucleation threshold is too high (some Torr) to occur in the earth's atmosphere. Thus another nitrogen compound must be involved if one assumes that some nitrogen compound condenses directly together with water vapor without requiring the presence of previously formed aerosols. As a possible candidate for the earth's stratosphere, Kiang et al. (1973*c*) propose a nitrogen compound of low volatility, e.g. the addition compound $NH_3 \cdot SO_2$ (see also the paper of McLaren et al. in this conference) requiring even at low relative humidities a partial pressure around 10^{-7} Torr only (near -70°C). Other possible candidates in the earth's troposphere are $(NH_4)_2SO_4$, NH_4Cl, and NH_4NO_3 for heteromolecular nucleation together with water. The situation may be different in the atmosphere of other planets (work to be published in "Icarus"); e.g. Jupiter's air contains a lot of NH_3.

This nucleation process is one intermediate step in the total gas-to-particle conversion process (Kiang et al., 1973*a*). Heteromolecular nucleation in the earth's atmosphere is preceded by (photo-)chemical reactions producing those low vapor pressure compounds which can nucleate under atmospheric trace gas concentrations; e.g. the high vapor pressure SO_2 gas is oxidized into the low vapor pressure H_2SO_4 gas. The nucleation of a small droplet is then followed by the growth of this droplet (heteromolecular condensation), by droplet coagulation, and by chemical reactions in the interior or on the surface of the droplet. The initial gas phase reaction, the heteromolecular nucleation process, and the later droplet growth are coupled together since they all influence the concentration of the condensable trace gas involved in the nucleation. An order of magnitude solution of these equations (Stauffer et al., 1973; H_2O–H_2SO_4 only) relates the number of nucleated droplets, their size (typically, 0.01 micron), and the time scales involved (typically: one minute) to the nucleation rates of Kiang et al. (1973*a*, *b*). Thus these calculations may be relevant for the size distribution of Aitken nuclei. They also facilitate comparison with experiment: We find the H_2O–H_2SO_4 droplet concentrations measured by Cox (this conference) to agree within a factor 10^3 with those predicted by Stauffer et al. (1973). (These calculations neglect coagulation effects and liquid phase reactions.)

This heteromolecular nucleation process (homogeneous or heterogeneous) is different from the heterogeneous homomolecular nucleation of pure water on an H_2SO_4 droplet, discussed by Vohra & Nair (1971) for large droplets. However, for relative humidities above 100%, our heteromolecular nucleation process can be followed by the Vohra–Nair heterogeneous nucleation of pure water (Stauffer et al., 1973).

Most of our calculated nucleation rates refer to homogeneous heteromolecular nucleation, i.e. without the presence of pre-existing large nuclei. If large aerosols are already present at the beginning, then heterogeneous heteromolecular nucleation may occur at much lower trace gas concentrations. But even in this case, the knowledge of homogeneous heteromolecular nucleation is necessary to predict under which atmospheric conditions new aerosols are formed homogeneously, and under which conditions only the pre-existing aerosols are enlarged heterogeneously (Stauffer et al., 1973).

We recommend further studies of aerosol distributions in the range of 0.1 micron and less, and more complete measurements of thermophysical mixture properties like the partial pressures and the surface tension (in particular the vapor pressure of H_2SO_4). Computer simulations (see, for example, Burton, 1973) of such mixture droplets would be highly desirable to check our thermodynamic nucleation theory.

We are grateful for collaboration with and information from V. A. Mohnen, J. Bricard, D. Vigla, and R. A. Cox, and for support from NSF grant GA-33422 and NIH grant RR-8006.

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