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01 Jan 1971

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Recommended Citation

EXPERIMENTAL AND THEORETICAL STUDY OF THE SIGN PREFERENCE IN THE NUCLEATION OF WATER VAPOR*

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Abstract—The nucleation of water vapor on ions in atmospheres of helium and argon was studied using an expansion type cloud chamber. Separation of the positive and negative ions was achieved so that the nucleation could be studied as a function of both the sign of the ionic charge and the supersaturation.

A semiphenominological theory was developed as an extension of the classical liquid drop theory to include the effects of the ionic charge on the nucleation process. The theoretical model of the pre-nucleation embryo was assumed to possess an oriented dipole surface layer with the direction of orientation dependent on the sign of the ionic charge. The theory predicts not only the increase in the nucleation rate compared to that for homogeneous nucleation and a difference in rate between positive and negative ions, the negative ions having the higher nucleation rate, but also predicts a correction term to the classical theory of homogeneous nucleation for polar molecules which exhibit an electrical double layer at the liquid surface.

Comparison of the theoretical and experimental results for nucleation on both positive and negative ions yields good agreement and indicates the prenucleation embryo is probably a tightly bonded highly structured cluster possessing an oriented dipole surface layer.

INTRODUCTION

THE CLASSICAL liquid drop theory of homogeneous nucleation, while understandably inadequate, is still the most convenient starting point for the development of any heterogeneous nucleation theory. The nucleation on ions is probably the simplest type of heterogeneous nucleation since it avoids the introduction of the unknown composition and surface properties associated with the foreign particle in most types of heteorgeneous nucleation. It appears, however, that a study of the nucleation on ions would provide additional insight into the structure of the prenucleation embryos by the interaction of the ions electric field with the molecules of the embryo.

DEVELOPMENT OF THE THEORY

The modification of the classical liquid drop theory of nucleation (VOLMER and WEBER, 1926; FARKAS, 1926; BECKER and DORING, 1935; FRENKEL, 1939; ZELDOVICH, 1942) to the case of nucleation on ions by the addition of a single electrostatic correction term to the change in free energy of formation as proposed by such workers as THOMSON (1928), STACHORSKA (1965), and RUSSELL (1969) among others (FRENKEL, 1939; GLOSIUS, 1937), while predicting an increase in nucleation rates, can not predict a sign preference as shown by some polar substances such as water and alcohols (LOEB *et al.*, 1939). By assuming an oriented dipole surface layer for these substances (LOEB *et al.*, 1939; WEYL, 1951; GOOD, 1957; ABRAHAM 1968, 1969a, b; FLETCHER, 1962) and adding a surface dipole-quadrupole correction term (as suggested by FRENKEL, 1939) a sign preference can be predicted.

The theoretical model assumes a spherical liquid drop type prenucleation cluster with the ion at the center. The cluster surface is assumed to consist of a layer of oriented dipoles, with the direction of orientation governed by the sign of the ionic charge. To the expression for the change in free energy as used in homogeneous nucleation theory,

$$\Delta\Phi_H = -(\phi_A - \phi_B)g + 4\pi\sigma r^2, \tag{1}$$

must be added the standard electrostatic correction for the change in the field energy of the ion caused by the presence of the surrounding cluster:

$$\Delta\Phi_{ES} = -\frac{e^2}{2}\left(1 - \frac{1}{E_e}\right)\left(\frac{1}{r_e} - \frac{1}{r}\right) \tag{2}$$

where e is the ionic charge; ε_e, the effective dielectric constant of the cluster; r_e, the ionic radius; and r, the cluster radius. It has been assumed that $\bar{D} = \varepsilon_e \bar{E}$ in the cluster.

For a surface of oriented dipoles, such as assumed for the present theory, the molecular quadrupole moment of the surface molecules causes an energy difference between the two possible orientations of the dipoles normal to the surface. This difference in energy is due to the disruption of the dipole field's axial symmetry by the quadrupole field. The total molecular electric field is increased in one direction along the axis of the dipole and decreased in the other. When the dipole–quadrupole combination is on the surface between two media of different dielectric constants (ε_1 and ε_2), the resulting field energy is a minimum for the orientation which places the strongest part of the molecular field in the media of higher dielectric constant. Assuming for the purpose of calculating the dipole–quadrupole energy that to a first approximation the cluster surface can be treated as a plane surface, then the method of STILLINGER and BEN-NAIM (1967) can be used with the thickness of the surface reduced to zero. The dipole–quadrupole field energy, when the dipole moment is directed into the media of dielectric constant ε_1, is given by

$$W = \frac{3p^2}{a_0^3}\left[\frac{\varepsilon_1}{(1 + 2\varepsilon_1)^2} + \frac{\varepsilon_2}{(1 + 2\varepsilon_2)^2}\right] + \frac{75pQ_{zz}}{32a_0^4}\left[\frac{\varepsilon_1}{(1 + 2\varepsilon_1)(2 + 3\varepsilon_2)} - \frac{\varepsilon_2}{(1 + 2\varepsilon_2)(2 + 3\varepsilon_2)}\right]$$

$$+ \frac{1}{12a_0^5}[139Q_{zz}^2 - \tfrac{1}{9}(Q_{yy} - Q_{xx})^2] \times \left[\frac{\varepsilon_1}{(2 + 3\varepsilon_1)^2} + \frac{\varepsilon_2}{(2 + 3\varepsilon_2)^2}\right] \tag{3}$$

where p is the dipole moment, Q_{ii}, the elements of the diagonalized quadrupole tensor, a_0, the radius of a sphere of exclusion surrounding the point dipole–quadrupole combination to simulate the finite size of the surface molecule.

In the case of water the "normal" orientation of the surface molecules is with the dipoles directed into the liquid (WEYL, 1951; FLETCHER, 1962; STILLINGER and BEN-NAIM 1967) corresponding to $\varepsilon_1 = \varepsilon_e$ (the effective dielectric constant of the cluster) and $\varepsilon_2 = 1\cdot0$ (the dielectric constant of the vapor). Since this orientation occurs for both neutral and negatively charged clusters, it has been included as part of the macroscopic surface free energy. It is only the increase in energy due to the reversal of the surface orientation caused by the presence of a positive ion that must be added to the change in free energy for nucleation on positive ions. The energy difference per surface molecule is given by

$$\Delta W = \frac{75}{16}\frac{pQ_{zz}}{a_0^4}\left[\frac{1}{15} + \frac{\varepsilon_e}{(1 + 2\varepsilon_e)(2 + 3\varepsilon_e)}\right]. \tag{4}$$

Approximating the number of surface molecules by $g_s = (4\pi r^2)/(\pi a_0{}^2) = (4r^2)/a_0{}^2$,

the total increase in energy for a positive cluster over that for a negative cluster is

$$\Delta\Phi_{D-Q} = \frac{75pQ_{zz}}{4a_0^6}\left[\frac{1}{15} - \frac{\varepsilon_e}{(1+2\varepsilon_e)(2+3\varepsilon_e)}\right]r^2. \tag{5}$$

Since an oriented surface has been assumed for the cluster and the radius of curvature is small, a dipole–dipole surface correction to account for the nonparallel alignment of the surface dipoles has been included. This is the same term considered by ABRAHAM (1969b) only modified by use of FLETCHER's (1962) exponential decay of the degree of orientation with distance from the surface. This term is given by

$$\Delta\Phi_{D-D} = \frac{4np^2\cos^2\theta_0}{a^3}\left[\frac{(\alpha_0 - 1/2)^2}{\gamma}\right][1 - \exp(-2\gamma r/a)] \tag{6}$$

where n = number of nearest surface neighbors, α_0 = the orientation parameter (FLETCHER, 1962) γ = orientational decay parameter, (FLETCHER, 1962) a = dipole–dipole separation distance, and θ_0 = the angle between the dipole and the surface normal.

The total change in free energy is now given by

$$\Delta\Phi = -(\phi_A - \phi_B)g + 4\pi\sigma\mu^{2/3}g^{2/3} - \frac{e^2}{2}\left(1 - \frac{1}{\varepsilon_e}\right)\left(\frac{1}{r_e} - \mu^{-1/3}g^{-1/3}\right)$$

$$+ \frac{75pQ_{zz}}{4a_0^6}\left[\frac{1}{15} - \frac{\varepsilon_e}{(1+2\varepsilon_e)(2+3\varepsilon_e)}\right]\mu^{2/3}g^{2/3}\left[\frac{1+\delta}{2}\right]$$

$$+ \frac{4np^2\cos^2\theta_0}{a^3}\left[\frac{(\alpha_0 - \frac{1}{2})^2}{\gamma}\right][1 - \exp(-2\gamma\mu^{1/3}g^{1/3})a)] \tag{7}$$

where $\delta = \pm 1$ represents the sign of the ionic charge and the conversion for r to g is made by $r^3 = \mu g$, assuming $\frac{4}{3}\pi r^3 = v_B\,g$ (v_B = molecular volume in the liquid).

Using standard procedures such as given by FRENKEL (1939) a modified Kelvin–Thomson relation can be obtained.

$$kT\ln(S) = \frac{8\pi\sigma\mu^{2/3}}{3}g^{-1/3} - \frac{e^2}{6}\left(1 - \frac{1}{\varepsilon_e}\right)\mu^{-1/3}g^{-4/3}$$

$$+ \frac{25pQ_{zz}}{2a_0^6}\left[\frac{1}{15} - \frac{\varepsilon_e}{(1+2\varepsilon_e)(2+3\varepsilon_e)}\right]\mu^{2/3}g^{-1/3}\left[\frac{1+\delta}{2}\right]$$

$$+ \frac{8np^2\cos^2\theta_0}{3a^4}\left[\frac{(\alpha_0 - \frac{1}{2})^2}{\gamma}\right]\gamma\mu^{1/3}[\exp(-2\gamma\mu^{1/3}g^{1/3}/a)]g^{-2/3} \tag{8}$$

The change in free energy has not only a maximum representing the critical nucleus ($g = g_*$) but also a minimum corresponding to a small stable hydration cluster ($g = g_0$). The minimum might be used to estimate the mobility of cluster ions in damp gases.

From this point the expression for the change in free energy, equation (7) can be used in any of the various kinetic treatments to obtain a complete nucleation rate law. If Frenkel's procedure (1939) is used, the resulting rate law is given by

$$J = N_0\lambda_*\left[-\frac{\partial^2\Delta\Phi}{\partial g^2}/2\pi kT\right]_{g=g_*}^{1/2}\exp-\left[\frac{\Delta\Phi(g_*) - \Delta\Phi(g_0)}{kT}\right] \tag{9}$$

where $\lambda_* = 4\pi C_0 \mu^{2/3} g^{2/3} \beta$, β = number of collisions per unit surface area per unit time made by the vapor molecules, C_0 = the accommodation coefficient, and N_0 = the density of ions. For a more detailed treatment of the theory see WHITE (1970).

EXPERIMENTAL RESULTS AND CONCLUSIONS

The experimental work utilized the chamber (Fig. 1) and procedures used by Allen and Kassner (1969) with the addition of an X-ray apparatus to produce a narrow beam of ions in the chamber. A horizontal electric field was used to field separate the positive and negative ions permitting separate measurements on the two signs of ions. The X-ray beam was monitored by a scintillation counter to allow normalization of the ion densities produced in each expansion.
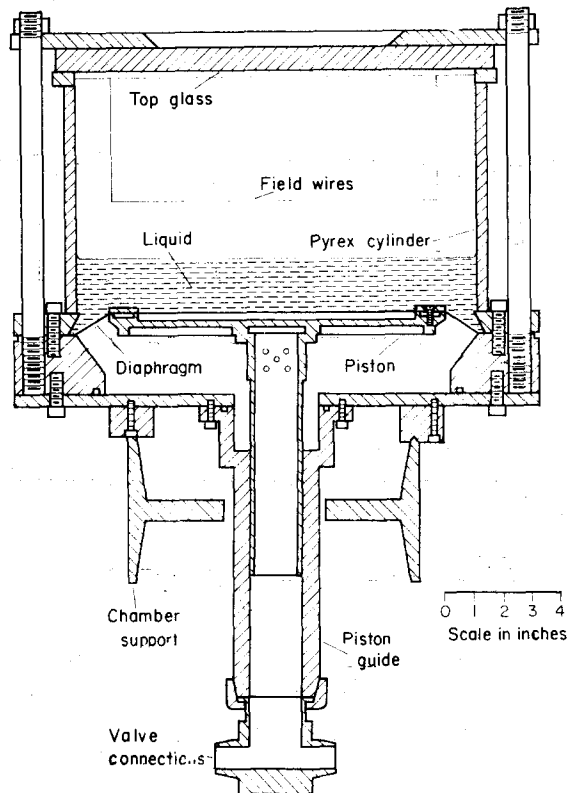

FIG. 1. Diagram of expansion cloud chamber.

The experimental results normalized to an ion density of 35 ions/cm^3 are shown in Fig. 2, plotting the total number of drops/cm^3 as the peak supersaturation of the expansion The curves are for positive and negative ions with argon and negative ions with helium as the carrier gas. Our previous observations that positive helium ions will not catal-yze the nucleation of water vapor were confirmed. The sensitive time for 90% of the nucleat-

ion was approximately 0·01 sec. The two solid lines in Fig. 2 represent the theoretical predictions for a parabolic pulse of supersaturation which closely approximates the chamber operating characteristics. The values used for the various parameters and physical constants are given in Table 1.

The present theoretical treatment is valid only for values of supersaturation below that value for which the two roots, g_0 and g_*, of equation (8) coincide. In using any kinetic treatment such as that by Frenkel in which exp $[\Delta\Phi(g_*) - \Delta\Phi(g_0)]/kT$ is approximated by a power series expansion in order to evaluate an integral, the approximation that the limits of the integration can be extended to $\pm \infty$ causes the result to break down at a maximum supersaturation where $g_0 = g_*$. In practice the limited number of ions present in the system will be completely depleted before the system can be brought to a super-saturation where the theory loses its validity.
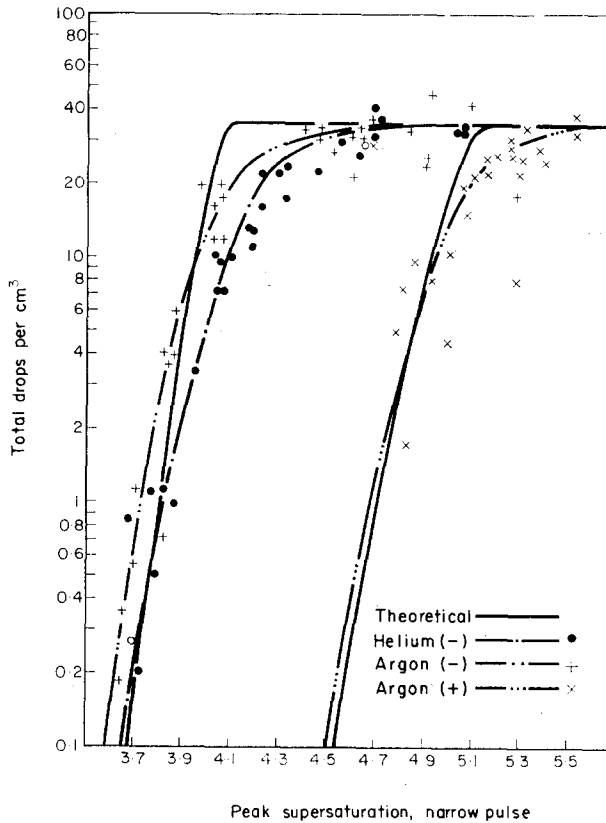

Peak supersaturation, narrow pulse

FIG. 2. Number of drops nucleated as a function of peak supersaturation. Initial temperature = 25°C.

TABLE 1. VALUES OF PARAMETERS AND PHYSICAL CONSTANTS USED IN THE THEORETICAL CALCULATIONS

$$e = 4 \cdot 8 \times 10^{-10} \text{ esu}$$
$$p = 1 \cdot 87 \times 10^{-18} \text{ esu-cm}$$
$$Q_{zz} = 0 \cdot 364 \times 10^{-26} \text{ esu-cm}^2$$
$$k = 13 \cdot 8 \times 10^{-16} \text{ erg/}^\circ\text{K}$$
$$\sigma = (116 \cdot 459 - 0 \cdot 149228 \times T) \text{erg/cm}^2 \ (T \text{ in } ^\circ\text{K})$$
$$a = 2 \cdot 76 \times 10^{-8} \text{ cm}$$
$$\theta_0 = 55^\circ$$
$$\gamma = 0 \cdot 074$$
$$\frac{(\alpha_0 - \tfrac{1}{2})^2}{\gamma} = 3 \cdot 4$$
$$n = 3$$
$$\mu = 7 \cdot 1382 \times 10^{-24} \text{ cm}^3$$
$$a_0 = 1 \cdot 86 \times 10^{-8} \text{ cm}$$
$$\varepsilon_e = 3 \cdot 4$$
$$C_0 = 0 \cdot 54$$

If the maximum supersaturation for which equation (8) has two real roots is exceded the theory predicts that there is no longer a metastable state existing and nucleation will procede governed only by the kinetics of supplying vapor to the ions.

The agreement between theory and experiments appears to be good evidence in support of the presence of an ordered surface for even small clusters of water molecules. The low dielectric constant ($\varepsilon = 3 \cdot 4$) which is close to the high frequency value of ice indicated that the entire prenucleation cluster possesses a high degree of structure permitting little contribution to the dielectric constant from molecular rotations. We believe that the failure of the positive helium ions to catalyze nucleation is probably due to some mechanism which prevents the initial hydration of the positive helium ions.

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