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# A Correction to Classical Homogeneous Nucleation Theory for Polar Molecules Exhibiting an Electric Double Layer at the Liquid Surface<sup>1</sup>

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An oriented dipole surface layer is added to the classical liquid drop model of nucleation to account for the surface behavior of substances having polar nonsymmetrical molecules. The preliminary treatment of the change in free energy as given by Abraham is modified to include Fletcher's exponential decay of the degree of orientation. An additional correction for the excess binding energy due to the presence of a foreign molecule in the prenucleation cluster is included to account for the inflections observed in the experimental results of Allen and Kassner. The resulting free energy of formation is combined with the kinetic treatment of Frenkel to obtain a nucleation rate law. The theoretical results are compared to the experimental results of Allen and Kassner as a function of both supersaturation and temperature. The agreement is good once the heterogeneous component is taken into account.

## INTRODUCTION

The theory of homogeneous nucleation developed by Volmer and Weber (1), Farkas (2), Becker and Döring (3), Frenkel (4), and Zeldovich (5), while understandably inadequate, predicts nucleation rates which are in reasonable agreement with experiments on the nucleation of water vapor. The vast majority of the experimental work done to date has been of the "critical supersaturation" type which determines the supersaturation at which nucleation becomes appreciable as a function of temperature. Allard and Kassner (6) have reexamined the experimental results of Wilson (7), Laby (8), Powell (9), Volmer and Flood (10), Madonna *et al.* (11), and Sander and Damhøhler (12), a correction for the chamber-sensitive time using Williams' (13) formula brings the results into substantial agreement with the experimental results of Allard and Kassner and calculations

based on the classical liquid drop theory (4).

The data of Allard and Kassner, as they point out, was of a preliminary nature and more extensive data have been obtained by Allen and Kassner (14) using the same basic chamber but with numerous improvements in temperature and pressure control and data-recording techniques. A plot of the data of Allen and Kassner (Fig. 1) giving the total drop concentration as a function of peak supersaturation shows a pronounced inflection occurring in the data for two of the four initial chamber temperatures and shows a strong indication in the data for the remaining two temperatures that the inflection would be present if the data were extended to higher drop concentrations. Allen and Kassner suggested that the inflection represents the depletion of a limited number of heterogeneous centers, possibly hydrogen peroxide formed in the chamber from water vapor by the action of cosmic rays. However, they did not carry out any calculations to

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test this hypothesis. The present work carries out such calculations and includes a correction for surface effects peculiar to polar substances which exhibit strong hydrogen bonding, such as water.

### THEORY

The present work accepts as a starting point the classical liquid drop theory as given by Frenkel (4) with all the inherent shortcomings associated with the application of macroscopic principles to what is essentially a microscopic many-body problem. The free energy of formation of the prenucleation cluster of molecules is then corrected for the excess binding of a foreign molecule and the correction to the surface free energy due to an oriented surface of polar molecules.

#### SURFACE DIPOLE-DIPOLE CORRECTION

Recent experimental and theoretical work has indicated that substances which consist of polar molecules and exhibit a strong tendency for hydrogen bonding develop an oriented surface layer in which the electric dipole moments of the surface molecules assume a preferred orientation with respect to the plane of the surface. This results in a surface of electric dipoles which have essentially a parallel alignment with respect to each other. The work of Good (15) with the surface entropy of liquids and the theoretical work of Fletcher (16) on water and ice both support the hypothesis of an oriented surface layer for water.

Assuming then that the surface of water consists of polar molecules with their electric dipole moments aligned, then the dipole-dipole interaction energy for parallel alignment has been measured as part of the macroscopic surface free energy, and no correction is necessary provided the parallel alignment is maintained. However, for small embryos, such as occur in prenucleation clusters, the small radius of curvature of the surface causes adjacent surface dipoles to be rotated with respect to each other, thereby destroying the parallel alignment and causing an increase in the interaction energy. This effect has been discussed by Abraham (17).

Following Abraham's treatment of the

dipole-dipole interaction, the increase in potential energy of two adjacent dipoles due to opposite rotation of  $\xi/2$  with respect to the bisector of the line joining their centers is  $\frac{1}{2}p^2(1 - \cos \xi)/a^3$ , where  $p$  is the magnitude of the molecular dipole moment and  $a$  is the dipole-dipole separation distance. The total increase in potential for the surface is given by

$$W_s = \frac{1}{2} \{p^2(1 - \cos \xi)ng_s/2a^3\}, \quad [1]$$

where  $n$  is the number of nearest surface neighbors,  $g_s$  is the number of surface molecules and the prefactor of  $\frac{1}{2}$  is due to assigning half the energy to each dipole in the pairwise interactions.

The number of surface molecules can be approximated by a simplified solid angle consideration as  $g_s = 4\pi/\omega_o \simeq 2/[1 - \cos(\xi/2)]$ , where  $\omega_o$  is the solid angle subtended by a surface molecule. Provided that  $\xi$  is small enough for the approximation  $1 - \cos \xi \simeq \xi^2/2$  to be valid, then the increase in potential energy can be written as

$$W_s = \frac{p^2n}{2a^3} \left( \frac{1 - \cos \xi}{1 - \cos(\xi/2)} \right) \simeq \frac{2p^2n}{a^3}. \quad [2]$$

Fletcher's (16) calculations indicate that the degree of orientation decays exponentially below the surface and the degree of orientation can be approximated by  $\alpha_m = \frac{1}{2} + (\alpha_o - \frac{1}{2}) \exp(-\gamma m) + \dots$ , where  $\alpha$  is the orientation parameter,  $\gamma$  is the orientational decay parameter and  $m$  is the number of layers from the surface. The effective dipole moment per molecule in the  $m$ th layer is then given by  $2p(\alpha_m - \frac{1}{2}) \cos \theta_o$ , where  $\theta_o$  is the angle between the dipole and the surface normal due to hydrogen bonding. The total change in the energy of formation is obtained by integrating  $W_s$  over all layers using the effective dipole moment.

$$\begin{aligned} \Delta\Phi_{DD} &= \int_0^m \frac{8p^2n}{a^3} \cos^2 \theta_o \left( \alpha_m - \frac{1}{2} \right)^2 dm \\ &= \frac{8p^2n}{a^3} \cos^2 \theta_o \int_0^m \left( \alpha_o - \frac{1}{2} \right)^2 \\ &\quad \cdot \exp(-2\gamma m) dm \quad [3] \\ &= \frac{4p^2n}{a^3} \cos^2 \theta_o \left( \frac{(\alpha_o - \frac{1}{2})^2}{\gamma} \right) \\ &\quad \cdot [1 - \exp(-2\gamma r/a)]. \end{aligned}$$

The classical expression for the free energy of formation of the prenucleation cluster must be corrected for the surface curvature of the oriented dipole surface by the addition of  $\Delta\Phi_{DD}$ .

#### HETEROGENEOUS CORRECTION

The shape of the experimental curves given by Allen and Kassner (14) indicate, as they point out, the possible presence of a neutral heterogeneous nucleation center whose initial concentration is temperature dependent. It was assumed that there could be present some chemically reactive species which bonds into the cluster structure. Since the initial concentration of heterogeneous centers can be approximated as 1.6 times the initial vapor pressure measured in mm Hg, the indication is that the hypothesized hydrogen peroxide formed from water vapor through the action of background cosmic radiation is a likely source of the heterogeneous centers. This is also the reasoning given by Allen and Kassner.

The effect of the presence of the foreign molecule in the cluster is to lower the free energy of formation by an amount equal to the excess binding energy of the foreign molecule. To a first approximation, it can be considered to be independent of the size of the cluster, particularly if the binding energy is due to nearest-neighbor interactions. Therefore, an additional correction,  $\Delta\Phi_{He}$ , to the classical free energy of formation is necessary in the case of the heterogeneous component.

The total corrected free energy of formation of the prenucleation cluster is given by

$$\Delta\Phi = (-kT \ln S)g + 4\pi\sigma\mu^{2/3}g^{2/3} - \Delta\Phi_{He} + \frac{4p^2n}{a^3} \cos^2 \theta_o \left( \frac{(\alpha_o - 1/2)^2}{\gamma} \right) \times \left\{ 1 - \exp \left( -\frac{2\gamma\mu^{1/3}g^{1/3}}{a} \right) \right\}, \quad [4]$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $S$  is the supersaturation ratio,  $\sigma$  is the macroscopic surface free energy,  $g$  is the number of molecules in the cluster, and  $\Delta\Phi_{He}$  is zero for homogeneous nucleation and a positive constant for the

form of heterogeneous nucleation hypothesized by Allen and Kassner.  $\mu$  is a proportionality constant relating the radius of the cluster to the number of molecules;  $r^3 = \mu g$ , assuming that  $\frac{4}{3}\pi r^3 = v_l g$ , where  $v_l$  is the molecular volume in the liquid.

#### NUCLEATION RATE

Using the same procedure as given by Frenkel (4) a modified Kelvin-Thomson relation can be obtained resulting in

$$kT \ln S = \frac{8\pi\sigma\mu^{2/3}}{3} g^{-1/3} + \frac{8p^2n}{3a^4} \gamma \cos^2 \theta_o \mu^{1/3} g^{-2/3} \times \left( \frac{(\alpha_o - 1/2)^2}{\gamma} \right) \cdot \left\{ 1 - \exp \left( -\frac{2\gamma\mu^{1/3}g^{1/3}}{a} \right) \right\}. \quad [5]$$

This equation can not be solved for  $g$  in closed form, but for given values of  $T$  and  $S$  computer techniques can be used to obtain the critical cluster size,  $g^*$ . Continuing to follow Frenkel's treatment the nucleation rate,  $J$ , is given by

$$J = N_o \lambda^* \left( \frac{-\partial^2 \Delta\Phi^*}{2\pi kT} \right)^{1/2} \exp \left( -\frac{\Delta\Phi^*}{kT} \right), \quad [6]$$

where  $\Delta\Phi^*$  and  $(\partial^2 \Delta\Phi^*)/\partial g^2$  are the free energy of formation and its second partial derivative with respect to  $g$ , both evaluated at  $g = g^*$ , the critical cluster size.  $\lambda^* = 4\pi\mu^{2/3}\beta$ , where  $\beta = C_o p / (2\pi m k T)^{1/2}$  with  $p$ , the vapor pressure,  $m$ , the mass of a vapor molecule and  $C_o$ , the accommodation coefficient. For the case of true homogeneous nucleation  $N_o$  is the monomer concentration and  $\Delta\Phi_{He}$  is zero while for the heterogeneous nucleation  $N_o$  is the density of foreign molecules and  $\Delta\Phi_{He}$  is a positive constant.

#### EXPERIMENTAL METHOD

The experimental data was obtained using an expansion cloud chamber. The chamber is relatively large (approximately 14 in. diameter and 5 in. height) which gives it a relatively small surface-to-volume ratio and

a correspondingly long natural sensitive time. In order to more accurately define the sensitive time the chamber was partially re-compressed after the initial expansion to artificially terminate the sensitive time of the chamber before wall effects could disturb the central regions of the chamber. A detailed discussion of the procedure is given by Allen (18). All calculations of temperature and supersaturation were based on continuous readings of the pressure so that the compressive effect resulting from heat conduc-

tion from the walls would be automatically taken into account.

#### RESULTS AND CONCLUSIONS

The experimental data which plot the total density of drops as a function of peak chamber supersaturation for four different initial temperatures is shown in Fig. 1. The sensitive time of the chamber is a constant for all data. Moreover, 90% of the nucleation occurs during the relatively flat portion at the peak of the curve representing the

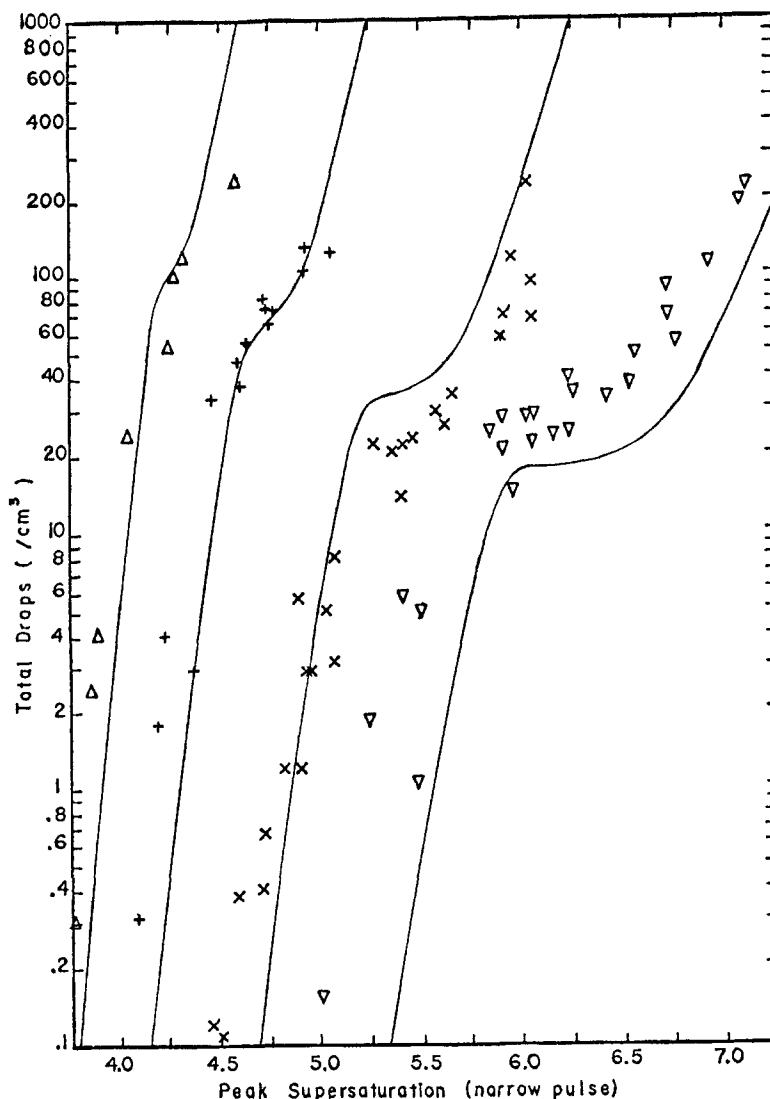


FIG. 1. Nucleation of water droplets from a helium atmosphere saturated with water vapor at four different temperatures:  $\nabla$  12.5°C,  $\times$  22.5°C,  $+$  32.5°C, and  $\Delta$  41.0°C.

supersaturation as a function of time. Therefore, the corresponding data for nucleation rate vs. supersaturation has essentially the same form as the data in Fig. 1. Vapor-depletion effects never amounted to more than a few per cent, an amount less than the probable error from other sources.

The curves represent the values obtained by numerically integrating the theoretical rate law over a pulse of supersaturation which closely approximates the chamber operation. The initial density of foreign molecules was taken as 1.6 times the initial vapor pressure in mm Hg and depletion of the foreign molecules by nucleation was accounted for during the numerical integration. Values of the various physical constants and parameters are given in Table I.

In calculating the theoretical results shown in Fig. 1, the temperature was treated as a function of the supersaturation such that the relationship between the two duplicated that which occurred in the experiments. The four curves represent an initial total pressure of 1185 mm Hg and initial temperatures of 12.5, 22.5, 32.5 and 41.0°C.

There is good agreement between the slopes of the theoretical and experimental results with both of them showing an increase with increasing temperature. There is also good agreement between the absolute magnitudes of the theoretical and experimental results. The decreasing offset at the inflection for increasing initial temperature is shown in both the theoretical and experimental results. The relative location of the calculated inflection point compared to the experimental results indicates that while a linear relationship between initial vapor pressure and density of heterogeneous centers is a good first approximation, the true relationship is undoubtedly more complicated; however, the accuracy of the present results does not warrant the use of a more complicated relationship.

Considering the approximate nature of the classical liquid drop model, the agreement between the theoretical calculations, using the corrected theory, and the experimental data is extremely good. At present it is impossible to identify the heterogeneous component and one can only speculate as to

TABLE I  
VALUES OF PARAMETERS AND PHYSICAL  
CONSTANTS USED IN THE THEO-  
RETICAL CALCULATIONS

$p = 1.87 \times 10^{-18}$ esu-cm
$k = 1.38 \times 10^{-16}$ erg/°K
$\sigma = (116.459 - .149228 \times T)$ erg/cm <sup>2</sup> ( $T$ in °K)
$a = 3.97 \times 10^{-8}$ cm
$\theta = 55^\circ$
$\gamma = .074$
$(\alpha_0 - \frac{1}{2})^2/\gamma = 3.4$
$n = 3$
$\mu = 7.1382 \times 10^{-24}$ cm <sup>3</sup>
$C_0 = 1.0$
$\Delta\Phi_{He} = 1.569 \times 10^{-12}$ ergs
$m = 2.99 \times 10^{-23}$ gm

its identity. One possible candidate is hydrogen peroxide as suggested by Allen and Kassner. Hydrogen peroxide is suggested for several reasons: first, its bonding is favorable for replacing two water molecules in the clathrate structure proposed for water clusters by Dace *et al.* (19), second, it could be generated in the equipment by the action of background radiation which accounts for the plateau being independent of the purification procedure used for the water, an effect observed in this laboratory over a period of years, and finally, the temperature dependence to a first approximation is proportional to the initial vapor density. Very tentative calculations of the normal mode spectrum for a clathrate structure of water molecules indicate that the replacement of two water molecules by a single hydrogen peroxide molecule causes a general stiffening of the structure and a shift of the normal mode spectrum to higher frequencies. At present, however, there are sufficient uncertainties in the theoretical molecular model calculation to prevent determining the energy change and comparing it to the  $1.569 \times 10^{-12}$  ergs required to obtain a fit between the experimental data and the theoretical calculations using the corrected theory. The authors wish to stress that the purpose of the present paper is to point out the existence of a heterogeneous component and not to identify it.

The present results, while not conclusive, support the nucleation model assumed in this

work. However, it should be noted that the molecular modeling approach presented by Dae *et al.* (19) may very well be able to account for the presence of the inflections without requiring the presence of a foreign molecule. Work is presently underway in this laboratory to extend the range of the experimental data to higher drop densities and lower initial temperatures, thereby extending the range of comparison between theory and experiment.

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