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Theory of vapor phase nucleation in binary mixtures of water and sulfuric acid*

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An expression for the nucleation rate of a binary vapor mixture of H_2O and H_2SO_4 at 25°C is derived which explicitly considers the contribution of H_2SO_4 hydrates to the droplet growth process. The continuum approximation used in earlier binary rate treatments has been abandoned in favor of treating the droplet composition in a discrete fashion. Rates of nucleation are calculated for a H_2O - H_2SO_4 vapor mixture at 50%, 200%, and 300% relative humidities for various H_2SO_4 vapor activities. A finite nucleation rate is predicted with a relative humidity of 50% and a monomer H_2SO_4 vapor activity of 10^{-3} . This translates to a vapor pressure of monomer H_2SO_4 of 3.6×10^{-7} mm Hg or 0.5 ppb of pure H_2SO_4 at 1 atm. At higher relative humidities (i.e., 300%), a finite nucleation rate is predicted for monomer H_2SO_4 concentrations of ~ 0.04 ppt. This represents a vapor pressure of 3.2×10^{-11} mm Hg for monomer H_2SO_4 .

I. INTRODUCTION

The role of sulfuric acid in aerosol formation in moist air is a subject of increasing environmental interest. The current state of this field is summarized conveniently by Bricard *et al.*¹ Almost no truly quantitative understanding of the problem exists, although a wealth of reliable qualitative results is available. This situation in no way results from the inadequacy of investigators, but rather from the surprising complexity of the systems involved, the difficulty of establishing instrumental methods for observing individual events at levels approaching the molecular, and, when the atmosphere itself is concerned, the impossibility of accurately reproducing environmental conditions in the laboratory.

With so much effort focused on atmospheric pollution, it is natural to attempt a phenomenological understanding of the integrated system before concentrating research on its component parts. Thus, work in smog chambers, flow chambers, and cloud chambers, has been aimed more at producing complicated "smogs" and "clouds" than at generating chemical precursors for, and the production of, single aerosol particles. Chemical reactions, photolysis, radiolysis, nucleation, and growth are but a few of the processes that must be dealt with, and a synthesis, based on a study in which all are occurring simultaneously, has its limits in providing a firm understanding of individual mechanisms.

Despite the focus on the "whole" system, the last decade has seen definite progress in the examination of component processes under relatively well controlled conditions. Most of this progress has occurred in the fields of reaction kinetics and photochemistry, where it has become feasible to measure the rate constants for elementary reaction steps without interference from smog chamber walls, using fluorescence excitation techniques.² Considerable progress has also been made in the study of primary photochemical processes, for example in the photooxidation of SO_2 .^{3,4} As data on elementary rate constants have been accumulated, the computer has been used^{5,6} to exploit models based on large numbers of simultaneous differential rate equations, and methods have been developed for handling

"stiff"⁷ equations.

In addition, the molecular beam has been brought into play in order to study complex formation,⁸ condensation,⁹ and other elementary events connected, possibly, with aerosol formation.

A particularly promising tool appears to be the cloud chamber, which has been used in three variations, namely the expansion chamber,¹⁰ the flow diffusion chamber,¹¹ and the static diffusion chamber.^{12,13} In the first two modes, the emphasis seems, again, to have been on producing whole clouds under rather complicated conditions, followed by the use of light scattering and theory in an attempt to unfold the data. The flow diffusion chamber has the advantage of permitting the addition of nucleating agents of known composition and size distribution to the condensing medium, but the control can be good only at moderate supersaturation (< 1.5), since at higher supersaturation it must be almost impossible to filter out nucleating centers so as to provide a nucleus-free standard state to which known nucleating agents can be added.

The static diffusion chamber has been employed mainly in the study of homogeneous nucleation,¹²⁻¹⁴ in unary or one-component systems, and also in the study of condensation on ions,¹⁵ not to mention its original application in high energy physics. During the 1960's, Katz¹² refined it into a very effective tool for this purpose. The present authors are currently engaged in an attempt to apply it to a wider range of problems in physical chemistry, among them the study of the photooxidation of SO_2 and the mechanism of nucleation in binary mixtures of water and sulfuric acid. Our preliminary observations, coupled with a theory of hydrate formation published recently,¹⁶ suggest the appropriate mechanism for the nucleation of droplets in sulfuric acid-water mixtures. An early calculation indicates that H_2SO_4 at partial pressures as low as 10^{-9} – 10^{-8} mm Hg or less than 1 ppt (a probable atmospheric concentration),¹¹ is capable of nucleating air at 50% relative humidity. This conclusion was arrived at by Doyle¹⁷ on the basis of another mechanism related to a general theory of binary nucleation published earlier.¹⁸

Mirabel and Katz¹⁹ refined Doyle's calculation and, on the basis of a more realistic estimate²⁰ of the vapor pressure of pure sulfuric acid, decided that pressures in the range 10^{-7} – 10^{-6} mm Hg would be required. The mechanism described below also predicts nucleation in this higher range of partial pressure still typical of some atmospheric condition.

This is a very important conclusion, since considerable controversy exists¹ over whether H_2SO_4 at atmospheric concentrations can be the precursor to aerosol formation.

II. THEORY

In view of the general importance of the problem, and in preparation for the analysis of experimental data obtained in connection with our cloud chamber studies (to be reported in a later paper) on the photo-oxidation of SO_2 , we develop, in this paper, what we now feel to be a more adequate, even if not perfect, theory of nucleation for H_2SO_4 – H_2O mixtures.

The mechanism of nucleation, treated in Refs. 17–19, took no account of hydrate formation as described in Ref. 16. A good place to begin the exploration of the possible effects of hydrates is Fig. 8 of Ref. 16, which we reproduce here as Fig. 1. The surface depicted in Fig. 1 is a computer-generated three-dimensional perspective plot representing the reversible work W required to form a liquid drop containing n_1 molecules of H_2O and n_2 molecules of H_2SO_4 from an initially homogeneous vapor. The plot is drawn in such a manner that the viewer appears to be looking down on the surface at a polar angle ψ of 45° from the vertical axis, and an azimuthal angle ξ about this axis of 315° . The perspective corresponds to the observer being at a distance d four body diagonals away from the origin. These values of ψ , ξ , and d give the viewer the impression that he is sitting behind and above the origin, looking over the surface out into "left field." This surface corresponds to a temperature of 25°C , and to a relative humidity of 300% with acid (H_2SO_4) activity in the vapor of 10^{-3} . Such an acid activity translates into a partial pressure of H_2SO_4 equal to 3.6×10^{-7} mm Hg. The saddle point on the free energy surface in Fig. 1 occurs (according to Table I of Ref. 16) when the drop contains 1.66 molecules of H_2SO_4 and 6.93 molecules of H_2O . Once the saddle is reached, it is possible for the drop to increase in size by a process involving a decrease of free energy. However, that process may involve the addition of *acid* as well as water molecules!

For the particular conditions of Fig. 1 we show, in Fig. 2, the profile through the free energy surface along the grid corresponding to four acid molecules, i.e., the free energy of formation of a drop which always contains four acid molecules, and to which *only* water molecules are added as we move to the right, parallel to the water axis. We see from Fig. 2 that, as long as there are four acid molecules in the drop, the addition of water is always a downhill process. In this case, the drop can grow spontaneously through the addition of water molecules alone, *provided* no acid molecules are lost!

We can estimate the rate at which acid molecules are lost (or at least an upper limit to that rate) by considering the acid vapor pressure from the drop whose composition corresponds to the saddle point. This drop is in unstable *equilibrium* with its surroundings such that its acid vapor pressure is exactly 3.6×10^{-7} mm Hg. According to Table I of Ref. 16, the radius of this drop is $R = 5.594 \times 10^{-8}$ cm, and therefore its surface area $4\pi R^2$ is 3.932×10^{-14} cm². The rate (according to simple Maxwellian kinetic theory) at which gas molecules hit one square centimeter of plane surface is²¹

$$\phi = p / \sqrt{2\pi m k_B T}, \quad (1)$$

where p is the pressure, m the molecular mass k_B the Boltzmann constant, and T the temperature. Therefore the rate at which the drop at the saddle is hit (regarding its surface as plane) is $\phi 4\pi R^2$. If the reflection coefficient (sticking coefficient) is assumed to be unity, this is also the rate of evaporation. Setting $4\pi R^2 = 3.932 \times 10^{-14}$ cm², $p = 3.6 \times 10^{-7}$ mm Hg, $T = 298^\circ\text{K}$ or 25°C , and $m = 1.6 \times 10^{-22}$ g for H_2SO_4 , we get $\phi 4\pi R^2 = 2.9 \text{ sec}^{-1}$. Thus, on the average, 0.34 sec elapses before a molecule of H_2SO_4 evaporates from or collides with the drop. Making the same calculation for water at 300% RH shows that the corresponding time is only 7.53×10^{-10} sec. Thus, the drop interacts with $\sim 10^9$

FIG. 1. The free energy surface for H_2O – H_2SO_4 droplet formation at 25°C with $\text{RH}=300\%$ and $a_2=10^{-3}$. n_1 , the number of H_2O molecules, and n_2 , the number of H_2SO_4 molecules, range from 0 to 40 and 0 to 10, respectively, and increase in the direction indicated by the arrows. The maximum and minimum values of the free energy W are given on the plot. All the scales shown are linear. The projection of the path of minimum free energy through the saddle point is shown on the cube base. The ending of the solid line represents the saddle point. The viewing angles are $\psi=45^\circ$ down from the W axis and $\xi=315^\circ$ about the W axis.

FIG. 2. A two-dimensional profile from the surface in Fig. 1 with $RH=300\%$ and $a_2=10^{-3}$. The profile shows the free energy W of droplet formation for 4 H_2SO_4 molecules and up to 40 H_2O molecules.

H_2O molecules in the time between interactions with H_2SO_4 molecules. It may therefore always be regarded as being at equilibrium with respect to exchange with water molecules. Between exchanges with H_2SO_4 molecules, H_2SO_4 acts as though it were an *involatile* solute.

In the above, we have ignored the fact that most of the acid is bound in hydrates (Fig. 11, Ref. 16). The order of magnitude of the result would be the same, but we would have to consider the time between collision of the drop with hydrates rather than anhydrous H_2SO_4 .

The situation corresponding to Fig. 2 of Ref. 16 is interesting. Here we have acid activity $= 10^{-3}$ and $RH = 50\%$. The saddle point is located (Table I, Ref. 16) at a drop containing about 10 acid and 30 water molecules. Figures 3–5 of the present paper show cross sections of the free energy surface, parallel to the H_2O axis, corresponding to drops with 5, 10 (the saddle), and 12 H_2SO_4 molecules. We see that the drop moves up (in

FIG. 3. A two-dimensional plot of the free energy W of droplet formation for 5 H_2SO_4 and up to 240 H_2O molecules at $25^\circ C$ with $RH=50\%$ and $a_2=10^{-3}$.

FIG. 4. A two-dimensional plot of the free energy W of droplet formation for 10 H_2SO_4 and up to 240 H_2O molecules at $25^\circ C$ with $RH=50\%$ and $a_2=10^{-3}$.

the direction of increasing H_2SO_4) an increasingly broad valley. The valley can never vanish, no matter how broad it becomes, because the system is undersaturated both with respect to pure liquid water and pure acid. However, by adding acid molecules, larger drops can form, and once beyond the saddle, they are stable.

Doyle¹⁷ conjectured over this possibility and suggested that in the atmosphere, very small traces of H_2SO_4 would lead to the formation of submicroscopic drops of H_2SO_4 solution which, although beyond the saddle, would cease to grow because the acid supply would become exhausted. However, such particulates could serve as condensation centers for other vapors, e.g., olefins. In order for this situation to arise, however, finite rates of nucleation are required. Whether high enough rates occur at low values of RH and small partial pressures of acid is a quantitative matter which can only be resolved by a definitive experiment or a reliable theoretical analysis.

Our experiments thus far indicate that finite rates occur at RH values in excess of 100% and at quite small

FIG. 5. A two-dimensional plot of the free energy W of droplet formation for 12 H_2SO_4 and up to 240 H_2O molecules at $25^\circ C$ with $RH=50\%$ and $a_2=10^{-3}$.

concentrations of acid. They also occur at higher acid concentration and RH values less than 100%. The aerosol, described by Doyle, is difficult but probably not impossible to observe (if it occurs). However, it will require equipment designed especially for this purpose.

We can develop the theory, confirm it for $RH > 100\%$, and use it for prediction at $RH < 100\%$. Both Doyle¹⁷ and Mirabel and Katz¹⁹ have done this, ignoring hydrates, and using a continuum theory.¹⁸ Some modification is necessary when hydrates are present. Furthermore, at large values of RH, the saddle occurs at such small drop sizes that it is reasonable to take the discrete nature of drop composition into account. We now do this.

The symbol (i, j) indicates a drop composed of i water and j acid molecules. We then consider the following reactions around a "node" (i, j) :

In these reactions, we have used the symbol I to indicate *net* rates per cm^3 at which water molecules are added, and J for the *net* rates of acid addition. Net fluxes are positive to the right. In the steady state,

$$I_{i-1,j} + J_{i,j-1} = I_{i,j} + J_{i,j} \quad (3)$$

From simple kinetic theory,²¹ the net rate at which acid hydrates strike a drop (i, j) is

$$\nu_{i,j} = (8\pi kT)^{1/2} \sum_h \sigma_h \mu_h^{-1/2} N_h \quad (4)$$

where σ_h is the sum of the drop radius $R_{i,j}$ and the hydrate radius R_h , μ_h is the reduced mass of the drop i, j and a hydrate with the h H_2O molecules, and N_h is the number of hydrates with h H_2O molecules per cm^3 . The sum in Eq. (4) goes over all hydrate species. If we assume a sticking coefficient of unity, we may write

$$J_{i,j} = \nu_{i,j} f_{i,j} - \gamma_{i,j+1} f_{i,j+1} \quad (5)$$

where $\gamma_{i,j+1}$ is the rate of evaporation of H_2SO_4 from a drop $(i, j+1)$, and $f_{i,j}$ and $f_{i,j+1}$ are the concentrations of drops (i, j) and $(i, j+1)$, respectively.

Applying detailed balancing in the usual manner,²² $\gamma_{i,j+1}$ can be eliminated, and we obtain

$$J_{i,j} = \nu_{i,j} N_{i,j} \left(\frac{f_{i,j}}{N_{i,j}} - \frac{f_{i,j+1}}{N_{i,j+1}} \right) \quad (6)$$

where $N_{i,j}$ and $N_{i,j+1}$ are the equilibrium concentrations of drops. We have [Eq. (18), Ref. 16]

$$N_{i,j} = N [1 - (\theta/N_a)] e^{-W_{i,j}/kT} \quad (7)$$

where N is the concentration of water molecules in the vapor and N_a is the *total* concentration of acid molecules in and outside of hydrates. $W_{i,j}$ is the height on the free energy surface, e.g., Fig. 2, at the point (i, j) . Finally,

$$\theta = \sum_h N_h \quad (8)$$

where the sum goes over all hydrates. In fact N_h can be derived from Eq. (7) with $j=1$. Thus, $N_h = N_{h,1}$.

Because of valley walls $I_{i,j}$ eventually goes to zero for small enough and large enough values of i . This means that in the steady state,

$$J_j = \sum_i J_{i,j} = \sum_i J_{i,j+1} = J_{j+1} = J \quad (9)$$

where the definitions of J_j and J_{j+1} are obvious. Furthermore, if there is always local equilibrium as discussed above, with respect to the addition of water molecules, it follows that

$$I_{i,j} = 0 \text{ and } \frac{f_{i,j}}{f_{s,j}} = \frac{N_{i,j}}{N_{s,j}} \quad (10)$$

although, in general, $f_{i,j} \neq N_{i,j}$. We further define

$$f_j = \sum_i f_{i,j} \quad (11)$$

and

$$N_j = \sum_i N_{i,j} \quad (12)$$

and from Eq. (10) we thus have

$$\frac{f_{i,j}}{f_j} = \frac{N_{i,j}}{N_j} \quad (13)$$

Substituting Eq. (6) into Eq. (9) we get

$$J = J_j = \sum_i \nu_{i,j} N_{i,j} \left(\frac{f_{i,j}}{N_{i,j}} - \frac{f_{i,j+1}}{N_{i,j+1}} \right) \quad (14)$$

Then, using Eq. (13) in Eq. (14), we have

$$J = \left(\sum_i \nu_{i,j} N_{i,j} \right) \left(\frac{f_j}{N_j} - \frac{f_{j+1}}{N_{j+1}} \right) = \nu_j N_j \left(\frac{f_j}{N_j} - \frac{f_{j+1}}{N_{j+1}} \right) \quad (15)$$

where we have defined

$$\nu_j N_j = \sum_i \nu_{i,j} N_{i,j} \quad (16)$$

a quantity known from Eqs. (4) and (7). Equation (15), with J constant independent of j , is in the form of the usual expression for nucleation in a *one* component system, and one can solve for J in the usual manner.²³ Thus, we get

$$J = \left(\frac{f_1}{N_1} - \frac{f_l}{N_l} \right) / \left(\sum_{j=1}^{j=l-1} \frac{1}{\nu_j N_j} \right) \quad (17)$$

As usual, f_l/N_l is negligibly different from unity, and if l is chosen large enough, f_l/N_l may be taken as zero. This gives

$$J = \left(\sum_{j=1}^{j=l-1} \frac{1}{\nu_j N_j} \right)^{-1} \quad (18)$$

for the rate of nucleation, in droplets/ cm^3 sec.

In the next section we calculate values for J for various conditions of acid activity and RH. In particular we

discover, like Doyle¹⁷ and Mirabel and Katz,¹⁹ that even in undersaturated (RH as low as 50%) air and with very low partial pressures of H_2SO_4 , finite rates of nucleation are predicted. However, our theory accounts explicitly for hydrate formation and the noncontinuous nature of drop formation.

III. NUMERICAL RESULTS

To calculate the nucleation rate from the expressions in the preceding section, one needs first to calculate the free energy of formation of a cluster of H_2O and H_2SO_4 molecules. The free energy W can be written as

$$W = n_1(\mu_1 - \vartheta_1) + n_2(\mu_2 - \vartheta_2) + 4\pi r^2 \sigma, \quad (19)$$

where we have now assumed the liquid drop model. In Eq. (19), μ_1 and μ_2 represent the chemical potentials per molecule for H_2O and H_2SO_4 , respectively, taken in the bulk liquid phase; ϑ_1 and ϑ_2 represent the chemical potentials per molecule in the vapor; r is the radius of the drop; and σ is the surface tension, also taken for bulk solution. In Eq. (19), H_2SO_4 and H_2O are chosen as the independently variable components. The standard states are pure H_2SO_4 and pure H_2O . These states are consistent with the thermodynamic data available, and are used to compute the free energy of the drop. Partial molar free energies were obtained from the bulk solution data of Giauque *et al.*;²⁴ partial molar volumes used to compute the drop radius were derived from bulk solution density measurements tabulated in the *Chemical Engineers Handbook*²⁵; and the data for the surface tensions of H_2O - H_2SO_4 solutions have been published by Sabinina and Terpugaw.²⁶ To allow interpolation, these data have been fitted to a variety of polynomials in such fashion that the error due to curve fitting never exceeds 0.1%. A more detailed discussion of the free energy calculation appears in a previous paper.¹⁶

All calculations were performed on an IBM 360/91 computer. Relative humidities of 50%, 200%, and 300% were chosen since the first is representative of atmospheric conditions and the last two are representative of conditions used in our experiments. Calculations were made using a range of H_2SO_4 vapor activities a_2 for each relative humidity such that nucleation rates of ~ 1 drop/ cm^3 sec were obtained. The nucleation rate J was computed using Eq. (18). The variation of $\log J$ as a function of a_2 is presented in Figs. 6-8. We have included with each figure values of N_a , the total number of H_2SO_4 molecules per cm^3 . Notice that for each plot the limits of summation used in Eqs. (16) and (18) are given. These equations require that one perform a double sum whose exact upper limits are somewhat arbitrary. For a single-component system,²⁶ the limit is generally taken far enough beyond the free energy maximum so that the transition from one cluster to the next larger can be considered irreversible. By analogy, then, for a two-component system after the drops are sufficiently far past the saddle point, they can be considered to grow irreversibly. Thus, how far beyond the saddle point the sums are truncated is of interest and will be discussed in more detail in the following section.

FIG. 6. A plot of the logarithm of the rate of nucleation per cm^3 per second J against the activity a_2 of the H_2SO_4 vapor, at 25°C with RH=50%. N_a , the total number of H_2SO_4 molecules in the vapor, is given for various activities. Max H_2SO_4 and Max H_2O are the upper limits of summation in Eqs. (18) and (16), respectively.

IV. DISCUSSION

Since most of the H_2SO_4 molecules in a H_2O - H_2SO_4 vapor mixture are hydrated,¹⁶ it is important to realize the effect hydration has upon the nucleation rate. This effect is twofold. First, the presence of hydrates tends to increase the nucleation rate since fewer interactions between H_2SO_4 and H_2O molecules are required to produce a critical cluster. Each growing cluster, when acquiring a hydrate, adds not just one H_2SO_4 molecule, but a number of H_2O molecules at the same time. This effect is of kinetic origin and tends to increase the nucleation rate. The second effect is of a thermodynamic origin and acts to decrease the rate. The presence of hydrates has a stabilizing influence on the vapor. It is, in a sense, "buffered" by the hydrates. If one tries to increase the partial pressure of free H_2SO_4 , most of the slack is taken up through formation of more hydrates, and the partial pressure or activity a_2 of the free H_2SO_4 is increased only slightly. The thermodynamic factor far outweighs the kinetic, and the overall effect of hydrate formation is to reduce the rate of nucleation.

Mirabel and Katz have calculated the nucleation rate for a H_2O - H_2SO_4 vapor mixture, ignoring hydrates and using a continuum theory.¹⁹ For a relative humidity of 50%, they find a partial pressure of 3.07×10^{-7} mm of H_2SO_4 is necessary for a nucleation rate of 1 drop/ cm^3 sec. This partial pressure corresponds to 9.80×10^9 molecules of H_2SO_4 per cm^3 . Using Eq. (18), which

FIG. 7. A plot of the logarithm of the rate of nucleation per cm^3 per second J against the activity a_2 of the H_2SO_4 vapor at 25°C with $\text{RH}=200\%$. N_a , the total number of H_2SO_4 molecules in the vapor, is given for various activities. Max H_2SO_4 and Max H_2O are the upper limits of summation in Eqs. (18) and (16), respectively.

allows for hydrates and treats the cluster growth discretely, the partial pressure of unhydrated H_2SO_4 required for a unit nucleation rate at the same relative humidity is $3.02 \times 10^{-7} \text{ mm}$. Because of the formation of hydrates, the total concentration of H_2SO_4 molecules in the vapor phase, whether hydrated or not, cannot be computed directly from this partial pressure. Nevertheless, this number N_a is derivable by the methods in Ref. 16 and corresponds to 2.52×10^{10} molecules/ cm^3 . This higher total concentration of H_2SO_4 is due largely to the stabilizing influence of hydration. The effect of the discrete summation in Eq. (18) is expected to be most significant for large relative humidities (e.g., $>300\%$) when the critical cluster contains only a few molecules. Even though the total concentration of H_2SO_4 required when using Eq. (18) is approximately 2.6 times greater than that required by the continuum theory, it is significant that both concentrations are in the range which atmospheric H_2SO_4 concentrations may attain.¹

The expression for the nucleation rate in Eq. (18) displays an extremely sharp dependence upon H_2SO_4 concentration. In Fig. 6, which corresponds to a relative humidity of 50% , increasing a_2 from 8×10^{-4} to 9×10^{-4} (about $\sim 11\%$) increases the nucleation rate from 0.55 to 2.07 drops/ $\text{cm}^3 \text{ sec}$ (an increase in rate of about 280%).

If we consider Fig. 8, which corresponds to a relative humidity of 300% , we see that a rate of 1

drop/ $\text{cm}^3 \text{ sec}$ is achieved at an a_2 of about 9.00×10^{-8} . This corresponds to a total vapor phase concentration of acid molecules (hydrated and free) of $\sim 4.3 \times 10^7$ molecules/ cm^3 , which represents, at 1 atm total pressure, ~ 2 ppt. In terms of unhydrated acid concentration, it represents ~ 0.04 ppt. The dependence of the nucleation rate on activity is still very sharp. A 25% change in a_2 , in the neighborhood of a nucleation rate of 1 drop/ $\text{cm}^3 \text{ sec}$, produces roughly a 130% change in the rate.

As we have indicated, when performing the summations indicated in Eqs. (16) and (18), the choice of the upper limits is somewhat arbitrary. The summation in Eq. (16), along the grid lines, parallel to the water axis on the free energy surface, is usually carried out to, or slightly beyond, the free energy maximum for each grid line. This is not possible in every case, however, due to insufficient thermodynamic data. The chemical potentials required to compute the reversible work of formation and ultimately the nucleation rate have only been tabulated for solutions with at least $8.9 \text{ wt}\%$ H_2SO_4 . Those portions of the free energy surface with acid/water ratios less than about $\frac{1}{56}$ cannot be accurately calculated. If the barrier maximum along any water grid line corresponds to a cluster composition less than $8.9 \text{ wt}\%$ H_2SO_4 , Eq. (16) cannot be summed to the maximum. The effect of varying this upper limit of summation has been examined, and the results are given in Table I.

FIG. 8. A plot of the logarithm of the rate of nucleation per cm^3 per second J against the activity a_2 of the H_2SO_4 vapor at 25°C with $\text{RH}=300\%$. N_a , the total number of H_2SO_4 molecules in the vapor, is given for various activities. Max H_2SO_4 and Max H_2O are the upper limits of summation in Eqs. (18) and (16), respectively.

TABLE I. The change in rate of nucleation J in number of drops/cm³ sec for various values of Max H₂O and Max H₂SO₄, the upper limits of Eqs. (16) and (18), respectively. The values of J are calculated at 25 °C for three different free energy surfaces. Surface A corresponds to a relative humidity RH of 50%, and acid vapor activity a_2 of 1.0×10^{-3} , and an approximate saddle point composition of 30 H₂O and 10 H₂SO₄ molecules, respectively. Surface B corresponds to RH=200%, $a_2 = 5.0 \times 10^{-6}$, and an approximate saddle point composition of 29 H₂O and 5 H₂SO₄ molecules, respectively. Surface C corresponds to RH=300%, $a_2 = 1.0 \times 10^{-7}$, and an approximate saddle point composition of 24 H₂O and 3 H₂SO₄ molecules, respectively.

Free energy surface	Max H ₂ O (molecules)	Max H ₂ SO ₄ (molecules)	J (drops/cm ³ sec)
A	63	10	4.4
	120	10	4.4
	120	13	3.1
	120	20	3.0
B	63	6	18.7
	120	6	18.9
	240	17	18.3
	120	12	18.2
C	40	3	0.39
	63	3	0.49
	73	3	0.50
	120	3	0.55
	120	8	0.52

For a relative humidity of 50% and an a_2 of 10^{-3} , the saddle point on the free energy surface corresponds roughly to 30 H₂O and 10 H₂SO₄ molecules, respectively. Summing just to the saddle in Eq. (18), Table I shows that changing the summation limit in Eq. (16) from 80 to 100 has no noticeable effect on the rate. Excluding terms in the summations corresponding to acid/water ratios less than $\frac{1}{5}$ were found to have no observable effect on the calculated rate. The fact that the upper limit for the water summation has negligible effect on J is not surprising in view of the profile in Fig. 4. At the saddle there is still a very pronounced, although broad, free energy valley parallel to the water axis. The point on the grid line corresponding to 80 H₂O molecules is so far above the minimum that moving up the barrier to 100 H₂O molecules really has no significant effect. The net flow along this grid line is zero [e.g., $I_{i,j} = 0$ in Eq. (10)]. The assumption $I_{i,j} = 0$ begins to fail, however, if the upper limit in Eq. (18) is extended too far. The reason is suggested in Figs. 4 and 5. As one sums Eq. (18) to larger numbers of acid molecules, the barrier along the water axis decreases until a point is reached where the net flow $I_{i,j}$ is no longer zero. This effect becomes significant at high relative humidities (e.g., 300% and greater).

While it is important not to sum the number of acid molecules too far past the saddle, it is equally important not to truncate the sum too quickly. At the saddle point or slightly beyond, the probability of a cluster returning to a presaddle composition is considerably greater than at a point much further from the saddle. It is necessary, then, to sum over the number of acid molecules in Eq. (18) far enough so that the chance of a

cluster returning over the saddle is small. This is illustrated by the data in Table I for 50% relative humidity. Summing Eq. (18) to 11 acid molecules, e.g., to the saddle, gives a higher rate of nucleation than summing to 15; summing further to 17 does not change the nucleation rate significantly.

Proper choice of the summation limit becomes more critical at higher relative humidities. This is clear from the data in Table I corresponding to 300% relative humidity and $a_2 = 10^{-7}$. For these conditions the saddle point corresponds, roughly, to 3 H₂SO₄ molecules and 24 H₂O molecules. Summing Eq. (18) to 3 H₂SO₄ molecules and varying the upper limit of summation in Eq. (16) from 40 to 60 to 100 and finally to 120 H₂O molecules produces a significant variation in the rate. The reason for this lies in the fact that at this high relative humidity the barrier height along the H₂O grid line is lowered and the free energy valley broadened significantly with each added H₂SO₄ molecule. Summing to 40 or 60 H₂O molecules does not take one sufficiently far from the valley minimum. If the sum is carried to 120, we are now out of the valley and past the barrier maximum, so $I_{i,j}$ is roughly zero. However, one or two acid molecules beyond the saddle point, the barrier along the H₂O grid becomes nonexistent, and Eq. (18) is no longer applicable since the assumption of zero net flow along this direction, $I_{i,j} = 0$, is invalid. For this reason, at high relative humidities (e.g., 300% or greater) we have truncated the sum in Eq. (18) at the saddle point. However, this somewhat arbitrary convention must lead to a result of uncertain accuracy, and a proper theory would, instead, deal with the steady state condition in which the assumption $I_{i,j} = 0$ is replaced by

$$I_{i-1,j} + J_{i,j-1} = I_{i,j} + J_{i,j} \quad (20)$$

for each node (i,j) in Eq. (2).

Note added in proof: After submitting this paper to the Journal of Chemical Physics two publications on H₂SO₄-H₂O nucleation were brought to our attention.²⁷

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