AN EXPERIMENTAL STUDY OF GROWTH AND PHASE CHANGE OF POLAR STRATOSPHERIC CLOUD PARTICLES

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"An Experimental Study of Growth and Phase Change of Polar Stratospheric Cloud Particles"

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This reports progress made on understanding phase changes related to solutions which may comprise Polar Stratospheric Clouds. In particular, it is concerned with techniques for investigating specific classes of metastability and phase change which may be important not only in Polar Stratospheric Clouds but in all atmospheric aerosol in general. While the lower level atmospheric aerosol consists of mixtures of (NH₄)(SO₄)₂, NH₄HSO₄, NaCl among others, there is evidence that aerosol at PSC levels is composed of acid aerosol, either injected from volcanic events (such as Pinatubo) or having diffused upward from the lower atmosphere. In particular, sulfuric acid and nitric acid are known to occur at PSC levels, and are suspected of catalyzing ozone destruction reactions by adsorption on surfaces of crystallized particles. Such particles may result from water absorption by the acid aerosol followed by crystallization as hydrates or ice depending on temperature and composition.

A major question arises as to the extent to which such particles supercool (supersaturate) prior to crystallization, the nature of the crystallization itself in these droplets, and the nature of subsequent growth from the vapor of crystals in the form of ice or hydrate depending on the environmental conditions - temperature or vapor pressure (relative humidity). A crucial first question is the occurrence of solutions which supersaturate. It is well known (see Mason, The Physics of Clouds 1970) that aerosol particles in the lower atmosphere, of composition listed above, supersaturate substantially and
contribute to a hysteresis in visibility. The amount and time dependence of such metastability is ill understood, as is the dependence on insoluble aerosol (particularly soot) to nucleate such metastable particles, (Hallett, 1991). Identical questions occur for stratospheric clouds. The present study has centered on two approaches:

1) The extent of supercooling (with respect to ice) and supersaturation (with respect to hydrate) and the nature of crystal growth in acid solutions of specific molality.

2) The nature of growth from the vapor of HNO₃ - H₂O crystals both on a substrate and on a pre-existing aerosol.

1. Techniques:

The first class of experiment is designed to explore the range of supercooling (i.e. with respect to ice phase nucleation) of acid solutions of different concentration and temperatures down to -90°C. This was accomplished by observing cooling curves of approximately 1 ml solution in a glass test tube cooled slowly through the appropriate temperature of metastability. In practice, the approximate freezing (nucleation) point of each solution is determined; the final measurements were made for samples cooled rapidly to about 10°C above the expected nucleation temperature, then cooled slowly (1/100°C s⁻¹) until nucleation occurred. Such nucleation was readily detected by a sudden increase of solution temperature by latent heat release (Fig. 1). The nucleation was visible as ice crystals propagating through the solution. To each molality solution there is assigned an equilibrium freezing point depression (Table 1, 2). Above this temperature an inserted ice crystal will melt; below this temperature an inserted ice crystal will grow. This defines the concept of equilibrium freezing point, Figures 2, and 3 show the maximum supercooling obtained for
Figure 1(a) Cooling curve of 1 ml pure liquid water, showing the point of maximum supercooling and equilibrium freezing temperature.
Figure 1(b). Same as Figure 1(a) but, for 1 m HNO₃ solution.
| a | b | c | d | e | f | g | h | i | j | k | l | m | n | o | p | q | r | s | t | u | v | w | x | y | z |
| 0.50 | 1.0016 | 1.0039 | 5.0 | 0.051 | 79.6 | 1.7 | 6 | 1.3366 | 0.210 | 0.113 | 0.060 | 1.008 | 1.009 | 99.6 | 24.3 | 0.277 |
| 1.00 | 1.0049 | 1.0067 | 10.0 | 0.102 | 94.9 | 3.3 | 13 | 1.3342 | 0.423 | 0.227 | 0.122 | 1.017 | 1.016 | 98.5 | 47.8 | 0.573 |
| 1.50 | 1.0100 | 1.0118 | 15.0 | 0.154 | 99.7 | 6.6 | 25 | 1.3355 | 0.706 | 0.428 | 0.232 | 1.024 | 1.024 | 97.3 | 70.3 | 0.886 |
| 2.00 | 1.0151 | 1.0169 | 20.0 | 0.206 | 99.4 | 9.8 | 37 | 1.3361 | 1.004 | 0.540 | 0.293 | 1.044 | 1.043 | 95.5 | 113.1 | 1.58 |
| 2.50 | 1.0202 | 1.0220 | 25.0 | 0.258 | 98.6 | 13.0 | 47 | 1.3367 | 1.354 | 0.728 | 0.396 | 1.070 | 1.069 | 94.0 | 144.5 | 1.98 |
| 3.00 | 1.0253 | 1.0271 | 30.0 | 0.310 | 97.8 | 16.2 | 56 | 1.3373 | 1.855 | 0.998 | 0.543 | 1.097 | 1.096 | 93.4 | 194.9 | 3.57 |
| 3.50 | 1.0304 | 1.0322 | 35.0 | 0.362 | 96.9 | 19.4 | 67 | 1.3379 | 2.482 | 1.410 | 0.721 | 1.127 | 1.126 | 92.8 | 267.0 | 5.21 |
| 4.00 | 1.0355 | 1.0373 | 40.0 | 0.414 | 95.9 | 22.6 | 77 | 1.3385 | 3.341 | 2.020 | 0.908 | 1.157 | 1.156 | 92.1 | 347.5 | 7.67 |
| 4.50 | 1.0406 | 1.0424 | 45.0 | 0.466 | 94.9 | 25.8 | 88 | 1.3391 | 4.576 | 3.075 | 1.110 | 1.186 | 1.185 | 91.4 | 438.1 | 10.2 |
| 5.00 | 1.0457 | 1.0475 | 50.0 | 0.518 | 93.6 | 29.0 | 98 | 1.3397 | 6.551 | 4.559 | 1.323 | 1.212 | 1.211 | 90.7 | 537.6 | 12.8 |

Table 1 From Chemistry and Physics Handbook.
### Table 2

#### Nitric Acid, HNO₃

<table>
<thead>
<tr>
<th>Value of $Q_{0.05}$</th>
<th>Value of $Q_{0.10}$</th>
<th>Value of $Q_{0.95}$</th>
<th>Value of $Q_{0.99}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0010</td>
<td>0.0015</td>
</tr>
<tr>
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<td>0.0008</td>
<td>0.0012</td>
<td>0.0017</td>
</tr>
<tr>
<td>0.0009</td>
<td>0.0010</td>
<td>0.0014</td>
<td>0.0020</td>
</tr>
<tr>
<td>0.0011</td>
<td>0.0012</td>
<td>0.0016</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Note: Values of $Q_{0.05}$, $Q_{0.10}$, $Q_{0.95}$, and $Q_{0.99}$ are for all compounds.
Figure 2  Experimental Data for equilibrium freezing point (solid circles) and maximum supercooling (open circles) for increasing molality and known data from the Chemistry-Physics handbook (solid triangles) for ice-solution equilibrium point for H$_2$SO$_4$. 
Figure 3. Same as Figure 2 for HNO₃.
H$_2$SO$_4$, HNO$_3$. The maximum supercooling is represented by the open circles; it is demonstrated that there is a scatter of several degrees for each solution. The upper points (solid circles) represent the temperature reached by the solution within 1 to 5 s after the completion of the initial crystallization. This represents the equilibrium temperature of the solution after water has been removed by the crystallization, which enhances the concentration of the remaining solution. In the first instance we assume that the solid is pure ice, in which case all solute will be rejected, thus lowering the equilibrium melting point.

The solution cools through equilibrium (A Fig. 4) to become supercooled (B) whereupon it nucleates to increase in temperature and solution concentration (C). This process is near adiabatic as the heat transfer to the environment is small over the times required for crystallization. Subsequently the mix cools to the bath temperature, more ice forms and the solution becomes more concentrated (D). E represents the ice eutectic. The amount of ice formed initially will be by given the expression:

$$\int_{T}^{T_e} \frac{\sigma(T) \, dT}{L(T)}$$

where $\sigma(T)$ is the solution specific heat, $L(T)$ the latent heat - neither of which are well known for the solutions under study.

A parallel study is to investigate how the crystals grow - particularly the linear growth velocity. This is readily accomplished by making a VCR tape of the propagation of the crystallization front after nucleating the solution at a prescribed supercooling. The velocity is measured directly from the tape.
Figure 4: Schematic of conditions for nucleation of a supercooled solution. Arrows indicate solution temperature as it is cooled through the equilibrium point (A), nucleates at substantial supercooling (B) grows crystals adiabatically and concentrates (C) and finally equilibrates at the environmental temperature (D). The diagram beyond E (the ice - eutectic) represents the conditions for a hydrate which can experience the same process either side of the congruent melting point (MP).
For these solutions the viscosity increases substantially with decrease of temperature. At sufficiently low temperature, the growth velocity decreases until crystallization ceases. Figure 5 shows preliminary measurements; Figure 6 shows schematic of anticipated results from cruder qualitative measurements. This shows that a glass has formed. The results indicate that this happen for both acids under appropriate conditions. The above arguments all apply in the region of hydrate formation (i.e. to right of point E in Fig. 4), data in these regions is required.

2. Diffusion Chamber

Work is underway on the design and construction of a diffusion chamber to study aerosol and crystal growth directly (Fig. 7), temperature control will be by circulating bath and surface heater; the upper plate moisture/acid vapor source will be made of acid resistant stainless steel. The chamber walls will be made of acid resistant plastic. Temperature range, -90 to -60°C. Crystals will grow as indicated and examined by VCR; external aerosol will be injected as appropriate and examined for phase change (optical twinkling).
Figure 5. Measurements of ice crystal growth velocity in various molality of \( \text{H}_2\text{SO}_4 \) solutions. Degrees supercooling as for pure water below \( ^\circ\text{C} \).
Figure 6: Schematic of crystal growth velocity for H$_2$SO$_4$ solution characterizes the glass transition where $V = \text{zero}$, other than at the equilibrium melting point at high supercooling and high molality.
Figure 7: Diffusion chamber schematic. The walls are designed to withstand acid; the moisture source contains appropriate acid solution. The temperatures of top and bottom plates determine the mid temperature, the difference determines the mid level supersaturation. Crystals grow from the vapor on the central sting; otherwise aerosol is used from an outside source.
3. Initial Conclusions

The existence of the potential for substantial supercooling and a glass transition in polar stratospheric cloud particles opens new possibilities for surface chemistry. It would appear that the supercooled solutions might be less effective for a chemical reactions since the molecules would be more likely to enter the body of the solution. This will however depend on the self diffusion, which will fall as any glass transition is approached.

Equally important is that aerosol which is cycled through colder to warmer temperatures (as opposed to aerosol which goes from warmer to colder temperatures) will be more likely to form ice as hydrate clouds, since the glass will crystallize as its temperature is increased. Thus the behavior of a particle and its response to subsequent chemical reactions and cloud formation as it cools radiatively or by mountain were lifting may be determined by its previous history.

4. Continuing Work

- Repeat the supercooling experiments with smaller volumes (mm$^3$) to reach lower supercooling; extrapolate results to small aerosol values ($\mu$m)
- Explore the range of glass transition and measure growth velocities in greater detail, together with crystal shape.
- Examine the role of impurities (soot) on maximum supercooling.
- Extend studies to hydrate regions.
- Complete diffusion chamber and examine vapor growth in hydrate region.
5. References
