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AN EXPERIMENTAL STUDY OF GROWTH AND PHASE CHANGE OF POLAR STRATOSPHERIC CLOUD PARTICLES 145537

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N93-19887 0145537 Unclas 63/47 Ea AN EXPERIMENTAL CHANGE PHASE (Nevada STRATOSPHERI NASA-CR-192369) GROWTH 1991 Semiannua) Dec PULA C,

John Hallett Principal Investigator

and M.S. Student: Edward Teets

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Semiannual NASA report

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

By John Hallett and M.S. Student: Edward Teets

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 $(NH_4)(SO_4)_2$, NH_4HSO_4 , 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:

- 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 $HNO_3 H_2O$ 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.

89 SULFURIC ACID, H₂SO₄

MOLECUL	AR WEIGH	41 = 98.08	
RELATIVE	SPECIFIC	REFRACTIVITY	= 0.685

0.00 % hy will data are the same for all compounds.
For Values of 0.00 wt. 7, solutions see Table 1, Acetic Acid.

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App: Diff. Diff. Diff. N C Diff. N Diff. N Diff. N Diff. N Diff. N Diff. Diff. <thdiff.< th=""> <thdiff.< th=""> <thdiff.< t<="" th=""><th></th><th></th><th></th><th>C</th><th></th><th>ſ</th><th>IC - C I</th><th>(n - n)</th><th><u>_</u></th><th>Δ</th><th>0</th><th>s</th><th></th><th>910</th><th>ø</th><th>7</th><th>т</th></thdiff.<></thdiff.<></thdiff.<>				C		ſ	IC - C I	(n - n)	<u>_</u>	Δ	0	s		910	ø	7	т
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94.00 1812 1814 1721 17.50 104 888.3 96.00 1835 1.8394 1721 17.50 104 9 888.3 98.00 1836 1.8394 1794 18.346 36 961.5 100.00 1836 1.837 18.37 18.35 18.346 36 961.5	90.00	1.8144	1.8176	1633.0	16.650	1720	816.6										
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98.00 8361 8394 799 4 18.946 56 961.2 100.00 8305 8337 830.5 8.663 0.0 998.2	96.00	1.8355	1.8388	1762.1	17.966	71	924.8										
	100.00	1.8361	1.8394	1830.5	18.563		998 2										

Table 2

38 NITRIC ACID, HNO3

MOLECULAR WEIGHT = 63.02	
RELATIVE SPECIFIC REFRACTIVITY	= 0.818

	•	2.137			·· .	
0.00 % by will data are For Values of 0.00 wt	the sa	me for all utions see	compo Table I	unds. . Acetic	Acid	•• • • •

4%. N 141	D."	d D20	C, T	M g-mol 1	C.	-(C ₄ - C ₄) ∎1	(n − n _a) '⊭ 104	n	• C ·	Os kg	S S g-mol/1	9'4.	7 P cS	rhe	mmho'cm	g-mol
0.10	1.0009	1.0017	5.0	0.079	995.9	• 1	A ·	1 1 1 1 1 1	0 781	0.151	0.080	1.001	1 003	99.64		
1.00	1.0017	1 0054	10.0	0159	9916	4.6	11	1.33330	0.54	0.100	0 167	1.001	1.000	00 50	44.1	0.323
	1.0064	1.0081	151	0.240	991 1	6.9	01	1 1149	0 #17	0.300	0.102	1.003	1.000	99.40	90.1	0.000
1.00	1.0091	1.0109	יחי	0 120	988.9	9.1	26	1.3347	1 1 10	0.4.03	0.127	1.004	0.000	00.10	64.7	1.10
100	1.0110	1.0117	35.3	0 401	096.6	11.7	17	1 1147	1.120	0.001	0.327	1.005	0.007	00.17	108.	1.30
	1.0146	1.0164	10.4	0.483	484 7	14.0	10	1 1148	1.304	0.014	0.472	1.000	0.777	90.01	136.	1.97
1.40	1.0174	1 0197	35.6	0 565	981 8	16.5	45	1 1175	2 004	1.078	0 586	1.000	0.775	97.01	184	2.37
400	1.0202	1.0720	40.8	0.648	979 4	12.9	5	1 3381	2 315	1.345	0.500	1.017	0.775	90.03	104	5.10
4 50	1.0110	1 0248	46.0	0.710	976.9	21.3	58	1 3198	2.515	1415	0.0767	1.014	0.001	08.41	213.	4.3
100	10257	1.0176	51.3	0.130	974 4	21.5	64	1 1104	2.052	1.400	0.707	1.014	0.003	90.43	· · ·	,
50	10786	1.0304	56.6	0 898	972 0	16.3	1	1,1100	1 700	1 740	0051	1010	0.992	48.03		
A 181	10114	1 0337	61.9	0.981	969 4	78.7	78	1.3407	1 670	1.007	1049	1.010	0.97	40.02		
. 40	1.0347	1.0360	67.2	1.067	967.0	31.3	84	1.3414	1 974	7 1 1 7	1.144	1 020	0.991	97.84 97.59		
• nn	1 0170	1 0389	72.6	1.152	964.4	11.8	91	1 1471	4 177	7 176	1.741	1.075	0.991	47.04		
• 41	1.0399	10417	78.0	1 718	961.9	16.1	47	1 3477	4 687	2 5 2 0	1.340	1.019	0.000	47.30		
• (11)	1 (H27	1 0446	83.4	1 324	949 1	18.9	104	1 14 14	\$ 067	1 2 1	1 4 3 9	1 0 10	0.990	97 12		
• 41	1.0456	1.0475	88 9	1410	446 -	41.5	LIG	1 1440	541	141	1 5 18	1011	0 990	(A AU		
v nn	1.0485	1 0 504	94.4	1 497	441	44 1	117	1 3447	5.81	111	1 6 1 9	1.036	0.990	46.25		
• • 1	1.0514	1.0533	99.4	1.585	4414	46.7	174	1 3454	6.10	111	1 740	1 019	0.990	96.07		
n en	1.0543	1.0562	105.4	1.673	44R 9	49.4	130	1 3460	6.60	1 55	1 841	1041	0.440	95.79		
	1.0602	1.0620	116.6	1.850	941 5	\$4 7	144	1 1474	7.42	199	1045	1.049	(1991	9515		
00	1.0660	1.0679	127.9	2 0 10	418	60 1	157	1 1487	8 17	2.45	2 251	1.056	0.001	94.49		
1.00	1.0720	1 0719	119.4	2.211	4376	65.6	1.70	1 1500	415	447	1459	1.064	0.445	41 10		
4 (#)	10780	1.0799	150.9	2.195	41-1	717	184	1 1414	10.08	< a >	1 667	1071	ດີພະ	93.00		
• •	1.0840	1.0859	167.6	2.580	4114	76.8	198	1 1577	11.04	< vi		1.062	1.000	02.20		
•	1 (P#0)	1.0921	1-4-4	- 61	41.	× * <	211	1 1541	1104	6.1-	1.05	1.051	1.004	01.15		
	1 (1963	1.0982	186.4	2 457	404 4	88.3	225	1 3555	13.08	7.03	1.148	1 103	1.008	90.47		
• • • •	1.1025	1 1044	198.4	3 149	904.0	94.2	239	1.1569	14 16	~ ől	1 509	1 1 1 4	1 013	89 55		
	1.1087	1 1107	210.7	3 341	848 0	100.2	253	1 3582	15 30	8 22	1 7 20	11.76	1.018	88.60		
141	1.1150	11170	223.0	3 538	842.0	106 2	266	1 3596				1 1 3 4	1.014	87.67		
	1.1277	1.1297	248 1	1917	879 A	118.6	294	1 3624				1.167	1.037	85 55		
6.145	1.1406	1 1426	273 7	4 344	N04 .	1314	322	1 3652				1 197	1.052	×1 16		
	1.1536	1.1557	244.4	1749	x < 1 *	144 6	350	1 3680				1 231	1.069	81.06		
	1 1668	1.1688	326.7	5 1 84	840.1	141	378	1 3708				1 768	1 089	78 70		
(U)	E 1801	1.1822	354.0	5.618	826.0	172.2	406	1 1716				1 308	1.1.0	76 30		
•••	1 1934	1 1955	181 9	6 060	\$115	186.7	111	1 3763				1 141		71 87		
4 (#)	1.2068	1.2090	410.1	6511	746 5	201.7	460	1 1790				1 107	1.1.40	71.47		
L (B)	1 2202	1.2224	419 1	6 970	780.9	173	487	1 3817				1 4 4 7	1.190	49.04		
4 (#1	1 2335	1.2357	468 7	7 4 18	764 8	211.5	513	1 3847				1 501	1 100	64 50		
° (#1	1 2466	1 1489	449 7	7 91 1	748.0	150.7	637	1 1047				1.50	1 217	00,00		

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 H₂SO₄.



Figure 3. Same as Figure 2 for HNO_3 .



 H_2SO_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) represents 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:

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

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).



MOLALITY

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).

B		
24		
S C		
		2 M
		<u>3M</u>
	DEGREES SUPERCOOLIN	6

Figure 5. Measurements of ice crystal growth velocity in various molality of H_2SO_4 solutions. Degrees supercooling as for pure water below °C.

Figure 6: Schematic of crystal growth velocity for H_2SO_4 solution characterizes the glass transition where V = zero, other than at the equilibrium melting point at high supercooling and high molality.



SUPERCOOLING

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 <u>increased</u>. 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 (μm)
- 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

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