The Production of Condensation Nuclei by Crystallizing Salt Particles

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Abstract

Experiments were conducted to examine the possibility of condensation nuclei being produced by salt droplets when the environmental humidity was lowered sufficiently for crystallization to take place. It was found that condensation nuclei were in fact produced when salt particles crystallized, each salt particle producing at least several hundred nuclei. It is suggested that these nuclei consisted of minute salt crystals, with mass in the range 10^{-18} to 10^{-14}g, released from the main mass of salt during crystallization.

Introduction

DESSENS (1946) has reported that microscopic salt droplets may crystallize explosively when the environmental humidity is lowered, causing the nucleus to fracture into two or more visible fragments. LODGE and BAER (1954) recently reported experiments which led them to conclude that shattering of salt particles into fragments (greater than an unspecified detection limit) did not take place. On many occasions one of the writers has observed under a microscope the behaviour of salt particles when the environmental humidity is varied, and although crystallization has often been observed, on no occasion was visible frag-mentation noticed. However, it seemed possible that, during the crystallization of a large salt nucleus, very minute fragments might become detached, too small to be detected directly. Tiny particles of this kind should, however, be effective as condensation nuclei. It was hence decided to test this hypothesis by setting up an experiment in which an enclosed volume of air containing a few salt particles could be subjected to variations in relative humidity and its condensation nucleus content examined by adiabatically expanding the air and observing whether clouds formed on expansion.

Apparatus

In order to carry out this experiment, it was necessary to construct an apparatus in which a volume of air could be desiccated or humidified as required, without coming into contact with outside air or any other source of nuclei (chemical compounds or solutions, electric heating elements, etc.). Means also had to be provided for compressing and expanding the air and observing for cloud formation during adiabatic expansions.

The apparatus finally took the form shown in Figure 1. It consisted of an expansion chamber A, a drying chamber B and humidifier chamber C. Pressurization of the expansion chamber was accomplished by an airtight metal bellows which could be expanded by pressurizing it from an external source of compressed air. Chamber pressure was read on the gauge G. The air was dried by circulating cooled alcohol through coils within chamber B. The humidifier chamber C contained a small volume of water and could be warmed by an external heating element; the resulting increase in vapour pressure brought about an increase of relative humidity in the expansion chamber.

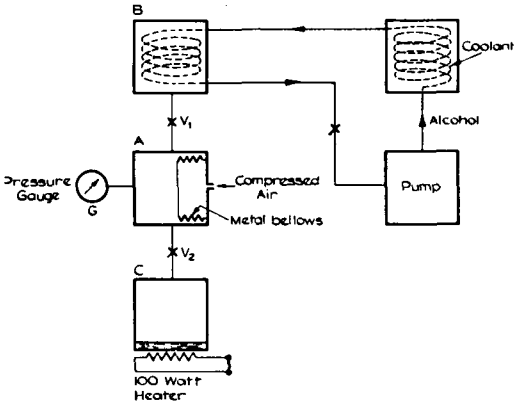

Fig. 1. Schematic representation showing the layout of the apparatus.

The cycle of operations was as follows:

(1) Filtered air was passed through the apparatus for some time before sealing.

(2) The air was humidified and any condensation nuclei remaining in the system were removed by successive adiabatic expansions.

(3) With V_2 closed, cooled alcohol was circulated through the drying chamber. A gradient of vapour pressure was thereby set up which gradually lowered the relative humidity in the expansion chamber. The relative humidity was measured by a metal-plastic dial hygrometer within the expansion chamber.

(4) When the required degree of desiccation was reached, V_2 was opened, V_1 closed, and the humidifying period begun. (The time variation of relative humidity during desiccating and humidifying periods is shown in Fig. 2(a) to 2(d).)

(5) When a relative humidity of 90 % to 92 % had been reached the air was subjected to an adiabatic expansion. Cloud droplets forming in the chamber could readily be observed in the intense heat-filtered beam from a mercury vapour lamp which illuminated the chamber at an angle of 150° to the direction of observation. The expansion ratio normally used represented a theoretical supersaturation in the chamber of 11 % (1·7° C).

Experimental

The actual experiments consisted of a series of tests following the operation cycle described above. Where salt particles were to be included in the expansion chamber, a spider web mounted on a perspex frame was sprayed with a concentrated solution of sea-salt and clipped to a removable panel in the expansion chamber.

In the absence of salt particles, nucleus-free

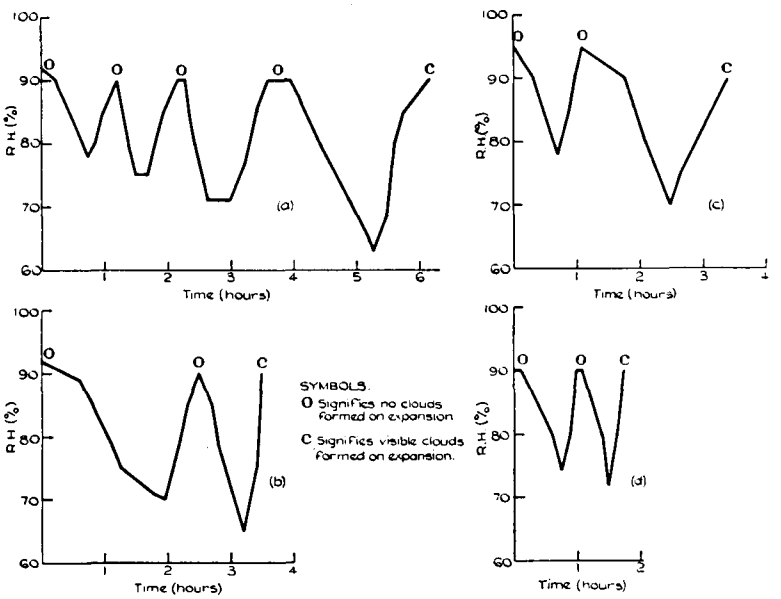

Fig. 2. Graphical illustration of the results of four experiments which were carried out to determine the threshold value of relative humidity for the appearance of nuclei in the chamber. Variation of R.H. with time is shown, and the results of adiabatic expansions are indicated at the appropriate points.

Table 1.

Experiment No.	1	2	3	4	5	6	7	8
Salt particles present	Yes	No	Yes	No	Yes	Yes	No	Yes
Initial R.H.	95 %	90 %	91 %	90 %	91 %	97 %	97 %	97 %
Period of desiccation (min.)	135	110	135	120	130	95	90	125
R.H. after desiccation	62 %	60 %	57 %	69 %	62 %	61 %	61 %	60 %
Period of humidifying (min.)	70	65	30	20	70	30	100	35
R.H. after humidifying	90 %	90 %	90 %	90 %	90 %	90 %	90 %	90 %
Expansion ratio (p_1/p_2)	1.042	1.042	1.042	1.042	1.042	1.042	1.042	1.042
Theoretical supersaturation	11 %	11 %	11 %	11 %	11 %	11 %	11 %	11 %
Cloud observed	Yes	No	Yes	No	Yes	Yes	No	Yes

air was dried to 60 % relative humidity, and then humidified. On expanding, no clouds were observed in the chamber. On the other hand, when salt particles had been introduced, fairly dense clouds were observed on expansion. A series of eight experiments in which salt was alternately included and omitted showed that nuclei were produced *only* when air *containing salt particles* was *desiccated*, humidified and expanded. An average of 20 expansions was required to clear the chamber of the clouds produced on these nuclei. These results are tabulated in Table 1.

Experiments were carried out to determine approximately the threshold relative humidity, to which the air containing the salt particles should be desiccated in order that nucleus production might take place. In these experiments, represented graphically in Figure 2, the chamber remained free of nuclei when the relative humidity had been lowered to 71, 70, 78 and 74 %, while nuclei were produced when the relative humidity had reached 63, 65, 70 and 72 % respectively. It is probable therefore, that the threshold for this effect was between 68 % and 72 % R. H. (The accuracy of the hygrometer was probably about ± 2 % R. H.)

An attempt was made to determine the critical supersaturation of the nuclei produced. It was not possible to determine this limit with accuracy, as the measurement of relative humidity within the chamber was liable to errors, and the characteristics of the expansion system with respect to deviations from the true adiabatic were not known. The theoretical supersaturation, deduced from temperature, humidity and critical pressure measurements was usually about 2·5 % (0·4° C), ranging from $<$ 1 to 11 % ($<$ 0·15 to 1·8° C) for individual experiments. Although the actual supersaturation would certainly have been smaller than the preceding adiabatic values, it seems likely that a supersaturation at least of the order of 0·2° C is necessary for these nuclei to grow to cloud droplet size. The relationship between nucleus size and critical supersaturation has been computed by many investigators (e. g. SQUIRES 1952). The following relationships are quoted for liquid drop nuclei and for hygroscopic salt nuclei.

Nucleus mass	Supersaturation for water droplets	Supersaturation for salt nuclei
10^{-11}g	0.1 % (0.015° C)	0.002 % (0.00025° C
10^{-14}g	1 % (0.16° C)	0.06 % (0.008° C)
01^{-17}g	12 % (1.85° C)	2 % (0.25° C)
10^{-20}g	300 % (19° C)	60 % (8° C)

It seems most likely, therefore, that the nuclei produced during the desiccation of salt particles are of the order of 10^{-14} to 10^{-18} g. It follows that a single salt particle of mass 10^{-10} g could produce several hundreds or more such nuclei without undergoing any appreciable reduction in size.

The density of the clouds observed in the chamber was of course somewhat variable, but a very conservative estimate of the droplet concentration would be 100 per cm^3. As the volume of air in the chamber was of the order of 1 litre and the number of particles on the spider webs seldom reached 100, it is seen that the crystallization of each salt particle must have produced many hundreds of minute nuclei.

A rough estimate of size was obtained by considering the velocity of fall of the nuclei when only a few were present in the chamber. The droplets formed on the nuclei fell out at

a few mm per sec, the supersaturation theoretically reached in the expansion being 1·7° C. This indicates that the nuclei had grown to a radius of 5 μ in about 1 sec. From theoretical computations of droplet growth (SQUIRES loc. cit.) it was found that to achieve this degree of growth, the nucleus mass should be greater than 10^{-18} g; the fact that the nuclei could remain in suspension in the chamber for an hour or so during humidifying periods suggested that their mass did not exceed 10^{-14} g.

Discussion

When a particle of sea-salt or common salt is placed in a stream of air whose humidity can be controlled, it undergoes a transition to the liquid state when the environmental relative humidity reaches 75 % (TWOMEY 1953, 1954). The relative humidity at which droplets of salt solution crystallize when the humidity is being lowered is not as well defined. This transition is of course dependent on the degree of supersaturation which the solution can tolerate and is probably critically dependent on the impurities present both in the solution and in the nearby air. During investigations in this Laboratory, it was observed that well-ventilated droplets 1 to 10 μ in radius usually crystallized around 70 % R.H. This figure agrees quite well with the threshold relative humidities at which condensation nuclei have been found to appear. It is therefore suggested that these nuclei were formed during the crystallization of the larger salt particles, and that they consisted of minute salt crystals released from the main mass during the crystallization process.

This result provides an alternative hypothesis for explaining the increased numbers of nuclei observed over land. It is not unreasonable to suppose that sea-salt nuclei travelling over land are subjected to greater and more frequent variations in environmental humidity than they are likely to encounter while over the ocean, so that the process of crystallization may at least partly explain the increase in the condensation nucleus count. The observations of CAUER (1949) concerning the escape of chlorine from droplets of salt spray (which CAUER attributed to a photochemical reaction) might well be explained by the release of condensation nuclei from crystallizing salt droplets.

It should be pointed out that the rate at which desiccation occurred within the expansion chamber (1 % to $^1/_2$ % R.H. per minute) corresponds to the rate of change of humidity occurring in the free air for adiabatic vertical movements with velocities which are quite low (less than 1 metre per second).

Conclusion

The crystallization of a few microscopic salt particles produces several hundred or more minute nuclei, which are effective condensation nuclei at moderate supersaturations. These nuclei are probably minute salt crystals with masses in the range 10^{-14} to 10^{-18} g.

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