Production of Ice Crystals in Air by a Pressure-Pack Method

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ABSTRACT

When a highly volatile liquid is sprayed into moist air the evaporation of the liquid droplets may cool the air sufficiently for the condensed water droplets to freeze by homogeneous nucleation. This paper describes the use of this technique to produce about 10^{10} ice crystals per gram of volatile liquid.

1. Introduction

When moist air is cooled to -40°C homogeneous ice nucleation takes place, an effect remarked on by Schaefer (1946) whose investigation resulted in the use of dry ice as a seeding material for cloud modification. The evaporative cooling of a volatile liquid can also produce ice crystals when the liquid is sprayed into moist air. Serpolay (1954) has used the liquid refrigerants methyl chloride and dichlorodifluoromethane (F-12) in this way. None of these materials are convenient to handle or store: dry ice requires considerable thermal insulation while the organic liquids have to be kept in pressure vessels. If the handling problems could be overcome the use of cooling reagents to produce ice nucleation would be useful in the laboratory as well as in the field because the number of ice crystals produced is high, e.g., 3×10^{10} per gm of dry ice according to Fletcher (1962), and the ice crystals are produced almost instantaneously.

This paper, therefore, examines the effect of cooling by highly volatile materials, especially liquids, in producing homogeneous ice nucleation in moist air, and describes a practical device for ice crystal production. Only liquids immiscible with water are considered, since it has been found (Fukuta, 1965) that water-miscible liquids do not produce ice crystals in this way.

2. Evaporative cooling by highly volatile liquids and homogeneous ice nucleation

The self-cooling ΔT of a falling droplet of diameter about 30μ is given by Green and Lane (1964) as

$$\Delta T = DLC/K,$$

where D , L , C and K are the diffusion coefficient of evaporating molecules, the latent heat of vaporization, the vapor density at the droplet surface and the thermal conductivity of the air, respectively. The cooling produced in falling drops of some common liquids of high

vapor pressure and low solubility in water are plotted in Fig. 1 against their vapor pressure at 0°C . The values have been calculated by a trial and error method and can be seen to fall close to a smooth line.

From the figure a liquid whose vapor pressure is about one atmosphere at 0°C is seen to give enough cooling to reach the temperature where the rate of homogeneous ice nucleation becomes observable. This was confirmed experimentally by spraying trichlorofluoromethane (F-11) or ethyl chloride.

In order to check the effect of further cooling on the number of ice crystals formed, mixtures of F-11 (trichlorofluoromethane or CCl_3F) and F-22 (chlorodifluoromethane or CHClF_2) were incorporated in small containers ("pressure packs" to which we will refer below) and tested by spraying into a cold box. As the vapor pressure of the mixture¹ at 0°C rose towards 2.2 atmospheres by increasing the proportion of the higher vapor pressure component F-22 from 0 to 40%, the number of ice crystals (determined by visual estimation) formed in a supercooled cloud of water at -10°C approached 10^{10} per gram of the mixture. Thereafter an increase of the vapor pressure to 4.8 atmospheres, that of pure F-22, was accompanied by little, if any, increase in the number of ice crystals. The spray droplet temperature of the 40% F-22, 60% F-11 mixture was calculated to be about -60°C . For comparison, the number of ice crystals produced by dry ice was found to be between 10^{10} and 10^{11} , and that by liquid air was about 10^{11} per gram.

The effect of water soluble vapor on homogeneous ice nucleation was tested by placing a concentrated ammonia solution at the bottom of a cold chamber whose temperature was adjusted to -15°C . After the ammonia had evaporated a mixture of 40% F-22 and 60% F-11 (both immiscible with water) was sprayed into the

¹ Estimated by applying Raoult's Law. Possible deviations of the calculated from the real values due to the mixture not obeying the law are not expected to be large.

of cold gas mixture containing its own vapor and air. The volume v may be estimated from the relation

$$v = L / \Delta T C_p \rho_g,$$

where L is the latent heat of vaporization of the liquid and may be taken as 100 cal gm^{-1} since only more or less non-polar materials immiscible with water are capable of inducing homogeneous ice nucleation. ΔT the amount of cooling required may be taken as 60°C . C_p and ρ_g are the specific heat and density, respectively, of the gas mixture which will be mostly air and hence the product $C_p \rho_g$ may be taken as $3 \times 10^{-4} \text{ cal cm}^{-3} \text{ deg}^{-1}$, thus

$$v \approx \frac{100}{60 \times 3 \times 10^{-4}} \approx 5.5 \times 10^3 \text{ cm}^3 \text{ gm}^{-1}.$$

Thus if we use Frey's value for the maximum droplet concentration we could expect 1 gm of volatile liquid to produce 10^{10} ice crystals and if we use a coagulation limited value of droplet concentration we could expect 1 gm of liquid to produce 2×10^{12} ice crystals. The maximum number of ice crystals we were able to produce experimentally with one gram of volatile material was 10^{11} with liquid air.

4. A practical form of ice crystal generator

We see now that there are theoretical reasons for our experimentally determined limit on the number of ice crystals that can be produced by spraying unit mass of volatile liquid into moist air; this limit can be achieved at about -60°C which is obtained by evaporating a liquid of 0°C -vapor pressure two to three atmospheres. This is just the range of pressure under which commercial "pressure pack" aerosol dispensers operate. These pressure packs consist of a metal container with a swirl atomizing nozzle on top of the valve system and containing the liquid to be sprayed and a propellant liquid of high vapor pressure.

In our case, where the primary aim is to produce by simple means a high concentration of ice crystals, we need to consider the toxicity, inflammability and temperature dependency of the vapor pressure of the liquids

used as well as the degree of cooling obtained. The latter is determined either by the selection of a single liquid or by the use of a mixture and varying the proportion of its components. When a mixture contains an appreciable amount of a low vapor pressure component, which itself is not able to produce temperatures less than -40°C , ice crystal production does not appear to reach the maximum. There is still, however, a large variety of combinations of liquids that can be used. A very suitable combination is the 40% F-22, 60% F-11 mixture mentioned earlier. These substances are non-flammable and non-toxic, and the pressure of the mixture is about 1.6 atmospheres at -10°C and about 5.6 atmospheres at 30°C . As we have seen above, this mixture will produce about 10^{10} ice crystals per gram, when released in a supercooled water cloud at -10°C .

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