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Occasional Report Number 6

PROJECT CIRRUS

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SCHENECTADY, NEW YORK

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GENERAL ELECTRIC

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Occasional Report Number 6

PROJECT CIRRUS

Variation with Temperature of the Nucleation Rate of Supercooled Liquid Tin and Water Drops

Prepared by

Bernard Vonnegut

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VARIATION WITH TEMPERATURE OF THE NUCLEATION RATE OF SUPERCOOLED LIQUID TIN AND WATER DROPS

A. INTRODUCTION

In investigations of the kinetics of the formation of a new phase, it is important to learn at what rate nuclei, or centers of formation for the new phase, make their appearance. It is possible to investigate the rate of nucleation by observing single masses of material during and after a phase transformation. However, in many cases it is difficult to separate the kinetics of nucleation from the kinetics of the growth of the new phase after nuclei have made their appearance. The nucleation of a substance can often be more easily studied by dividing it into a large number of small, mutually independent particles and observing as a function of time the number of particles which have undergone transformation. The time required for a particle to change from one phase to another once a nucleus has formed will, in general, be proportional to the first power of the particle radius. The chance that a nucleus will form will generally be proportional to the second or third power of its radius. Therefore, by making the particle sufficiently small, the time required for the occurrence of a nucleus can be made large in relation to the time required for the particle to transform once a nucleus has appeared. It is advantageous to make nucleation measurements on systems containing a sufficiently large number of particles to be easily treated statistically.

Preliminary investigations have been made on the nucleation of supercooled tin and supercooled water. Observations were made at constant temperatures on the freezing rate of systems composed of large numbers of supercooled drops.

B. EXPERIMENTAL METHODS AND RESULTS

1. Nucleation of Supercooled Liquid Tin

In the experiments on tin, the samples were prepared from a fine tin powder (obtained from Eimer and Amend) consisting of small spheres of tin ranging in diameter from approximately 1 to 10 microns. (The fact that the particles were far from uniform in diameter complicated the interpretation of experimental results. In future work, it will be desirable to perform the experiments on samples containing drops as nearly identical as possible.)

In the first experiments, the sample of tin powder was mixed with a bakelite varnish and spread as a film on a glass slide. The slide was mounted in a small electric furnace built to fit on a Philips x-ray diffraction apparatus. The apparatus was adjusted to give a strong diffraction line of the crystalline tin. The sample was then heated above its melting point (231.89°C) to 240°C. At the melting point, the diffraction line of the solid tin disappeared. Hydrogen gas was run through the furnace to prevent oxidation of the sample. After having been heated above the melting point, the sample was cooled and held at some temperature below its freezing point. The rate at which the supercooled particles crystallized was determined by measuring the rate at which the diffraction line of solid tin reappeared. The results of a typical experiment are shown in Fig. 1. It was soon found that the rate of nucleus formation was greatly increased by a small decrease in temperature and that the temperature control was not sufficiently sensitive to permit measurements with any accuracy.

A different apparatus was then set up in which the rate at which the tin particles solidified could be measured by the rate at which their volume changed. When liquid tin crystallizes, its volume decreases by about five per cent. The tin powder was first heated in air for about half an hour at 150°C to give it a thin coating of oxide to separate the particles. It was sealed into the bulb of a dilatometer (see Fig. 2). The dilatometer was then pumped out and baked at a pressure of less than a micron to remove any gas. "Octoil S" was then distilled into the dilatometer under vacuum. A

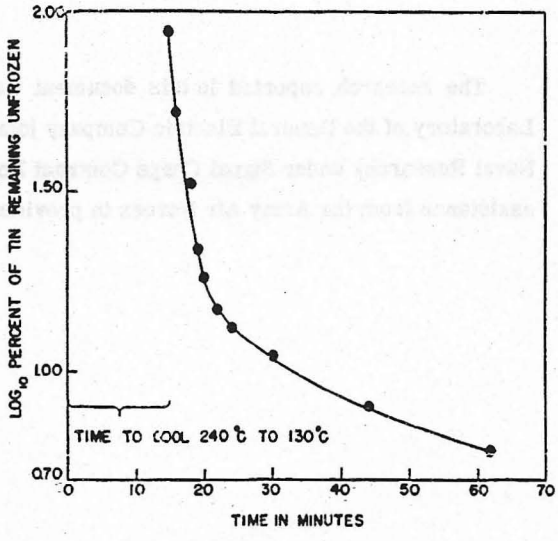

Fig. 1 Fraction of tin drops remaining unfrozen as function of time at 130°C from x-ray data.

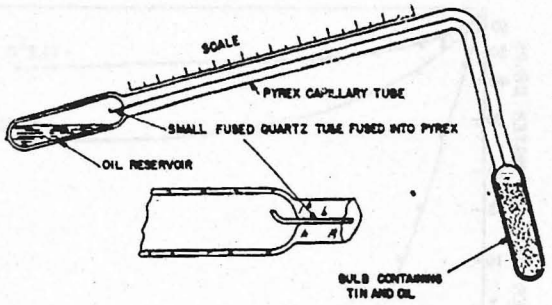

Fig. 2 Dilatometer.

measurement of the rate of nucleation was made by first heating the bulb to a temperature above the melting point of tin (265°C), and then placing it in a silicone oil, constant-temperature bath. The rate of nucleation was determined by observing the rate of volume decrease as measured by the motion of the "Octoil S" along a graduated capillary tube. A long capillary tube was used in the first experiments, but it was found that appreciable error was caused by the slow drainage of the liquid from the walls of the tube. This difficulty was minimized by using the oil reservoir shown in Fig. 2. During the melting of the sample, the tube was held at an angle so that the oil covered the end of the small fused quartz tube sealed into the pyrex capillary. (The small tube was made of fused quartz so that it would not melt while it was being sealed into the pyrex capillary). When the sample had been cooled to almost the desired temperature, the tube was tipped so that the excess liquid ran away from the end of the capillary tube, thus forming the meniscus in a convenient position.

The results of the experiments are shown in Fig. 3. The time has been plotted on a log scale to condense the curves for runs made over a long time interval. If the chances of a nucleus occurring in each tin particle were exactly the same and were independent of the length of time it had been supercooled, one would expect the rate of nucleation to decrease exponentially with time. The curves show clearly that in these experiments this is not the case. The fraction of the sample crystallizing per unit time steadily decreases with time. Some drops nucleate more readily than others, probably because they are either larger than the others or because they contain certain impurities which increase the probability of nucleus formation. The data obtained should be interpreted as the behavior of supercooled tin with whatever impurities were present. It is probable that tin, free of impurities, if it could be obtained, might behave very differently.

One of the most striking features of the data is the very great effect of temperature on the rate of nucleation. A decrease in temperature of seven degrees causes a sixtyfold increase in the nucleation rate. In observations on the rate of nucleation of supercooled water clouds in the presence of silver iodide smoke, the author has observed a similar large negative temperature coefficient(1). For a given smoke, the rate of ice crystal formation was approximately thirty times greater at -13°C than at -10°C.

An approximate value for the activation energy of the nucleation reaction can be computed from the data in Fig. 3. The log of the reciprocal of the time required for one third of the sample to freeze was plotted against the reciprocal of the absolute temperature to give the curve in Fig. 4. This corresponds to an activation energy of -2×10^5 calories. The data taken at 116.7°C has not been used because nucleation at that temperature proceeds so rapidly that most of the sample is frozen by the time its temperature has come to equilibrium with the constant temperature bath.

2. Nucleation of Supercooled Water

The author first attempted to measure the nucleation of supercooled water while conducting experiments at the De-icing Research Laboratory at M.I.T. An emulsion of water drops suspended in lubricating oil was cooled to -29°C with the expectation of measuring the nucleation rate by the rate of volume increase. This method was not successful because the solubility of water in the oil was sufficiently large so that diffusion rapidly took place from the unfrozen to the frozen drops.

Some preliminary studies on water have been made in this laboratory using a variation of the

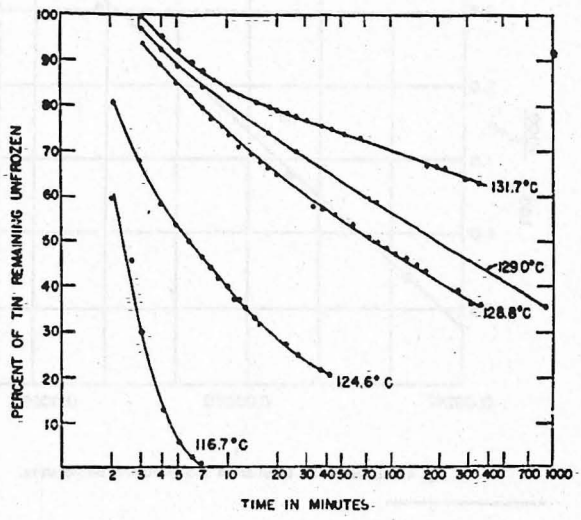

Fig. 3 Fraction of tin drops remaining unfrozen as a function of time from dilatometer data.

1. Vonnegut, B. To be published in CHEMICAL REVIEWS.

method described above. In these experiments, 64 drops of distilled water weighing approximately three milligrams each were placed in a square pattern on a polished chromium-plated metal plate.

On the recommendation of Dr. V. J. Schaefer of this laboratory, the chromium surface of the metal plate was covered with a thin film of polystyrene by dipping it into a solution. This had been found by Schaefer to lower the temperature to which the water could be supercooled. The plate with the drops on its surface was then placed on a thermostated copper block at some temperature below freezing. To prevent impurities in the air from settling on the water drops, the plate was covered with a piece of plate glass which rested on a raised rim on the copper block. The heat transfer between the block and plate was sufficient to bring the drops on the plate to the temperature of the block in less than one minute. The number of unfrozen water drops was measured as a function of time by visual observation. Figure 5 is a curve showing the nucleation of the drops at various temperatures.

Despite precautions to keep the water drops free from impurities, it is certain that the drops were contaminated by foreign material from the atmosphere and from the surface of the plate, which increased the rate of nucleation. Here again the data would probably be far different for completely pure water. The striking feature of the data is again the large negative temperature coefficient which characterized the results of the experiments on

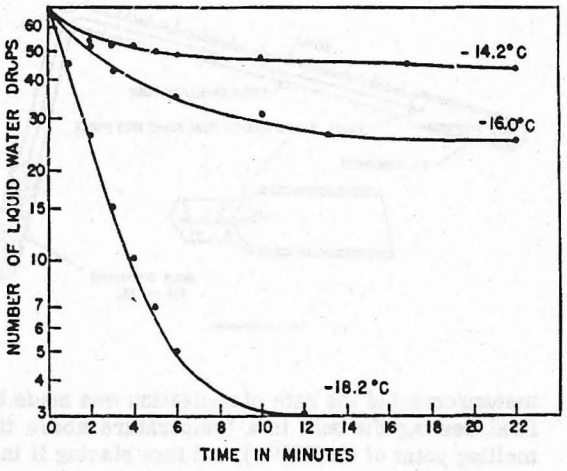

Fig. 5 Fraction of water drops remaining unfrozen as a function of time.

supercooled tin and on a supercooled cloud seeded with silver iodide.

The data for the freezing of water drops given in Fig. 5 can be interpreted in terms of the rate of nucleus formation per gram of water. Figure 6

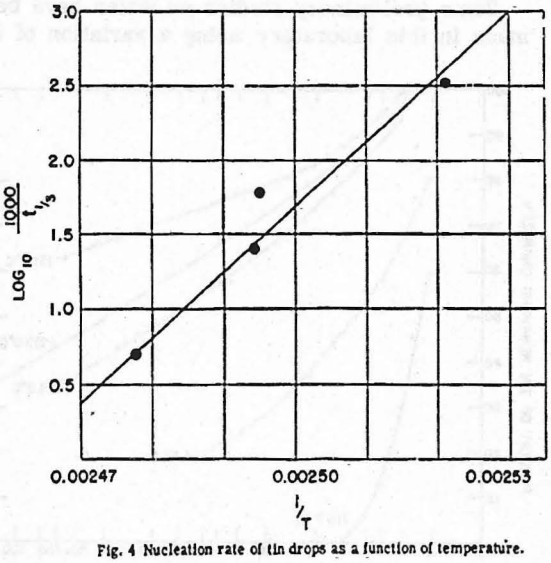

Fig. 4 Nucleation rate of tin drops as a function of temperature.

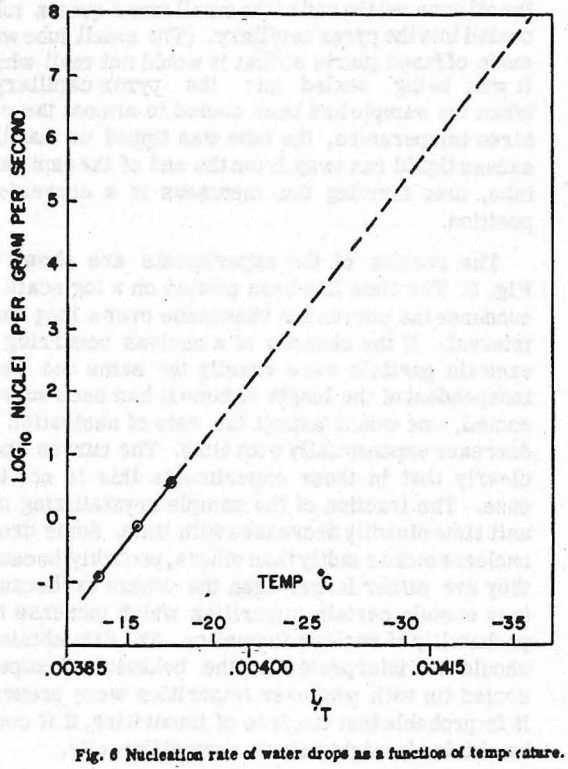

Fig. 6 Nucleation rate of water drops as a function of temperature.

2. Schaefer, V. J. SCIENCE, 104, pp. 457-459 (November 15, 1946).

3. Schaefer, V. J. BULLETIN OF AMERICAN METEOROLOGICAL SOCIETY, 29, No. 4, pp. 175-182 (April, 1948).

relates the rate of nucleus formation per gram to the reciprocal of the absolute temperatures. The rate of nucleation was calculated from the times required for the first 22 drops to freeze at the various temperatures. The energy of activation computed from the slope of the curve in Fig. 6 is -1.6×10^5 cal. It is interesting to extrapolate this data for comparison with observations made by Dr. V. J. Schaefer(2)(3) in his experiments on supercooled clouds. If it is assumed that the liquid water content in the cloud in the cold box is of the order of 1 gm/m^3, at a temperature of -25°C, according to this data ice crystals should be appearing at the rate of about 10^4 per second. Actually, with clean air at this temperature, no crystals are observed. It is not until the temperature falls below -39.0 +0.1°C that many crystals begin to form. The rate of nucleation in the water drops on the metal plate is much larger than that in the water drops in a cloud, probably because of the nucleating effect of the surface of the plate and chance impurities.

The sudden appearance of large numbers of ice crystals when the temperature is -39°C or lower indicates that in Schaefer's experiments the increase in nucleation rate with decreasing temperature must be even greater than that found in this work.

C. SUMMARY

X-ray diffraction, dilatometric, and visual techniques are described for measuring the extent of crystallization of systems composed of many small mutually independent volumes of supercooled liquid. Preliminary measurements on supercooled liquid tin and supercooled water show their rate of nucleation has a very large negative temperature co-efficient corresponding to an activation energy of the order of -2×10^5 calories.

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