An Interesting Case of Water Undercooling

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"If a pure liquid is carefully protected from mechanical disturbances, it may be cooled below the temperature at which it normally solidifies. Thus, water may be cooled to −10° C. or lower without becoming ice. The liquid at such a temperature is in a state of unstable equilibrium and will immediately solidify if disturbed or if a crystal of the solid is dropped into it" (*1*). Some such statement appears in physics texts when the subject of undercooling of a liquid is discussed. The difficulties of obtaining a successful mass demonstration of the undercooling of water are well known.

In investigations of the operating characteristics of home freezers in this Bureau, the tests include the freezing of a volume-capacity load with water as the test material in pint, paraffined, nested, cardboard containers with disc lids. Copper-constantan thermocouples are used with recording potentiometers. Since each instrument records its series of 16 points in approximately one minute, the temperature at each location can be followed quite closely.

Temperatures are taken in enough cartons, distributed throughout the freezing load, to be sure that they are obtained in the first and last cartons to freeze. In the case reported here, temperatures were taken in 7 of the 67 cartons comprising the full load. Undercooling occurred in 5 of these 7 cartons. If the phenomenon took place in the same proportion for all of the cartons, 48 of them undercooled.

The requirements generally stressed in textbooks for the phenomenon of undercooling are purity of liquid, absence of foreign substances, and absence of mechanical disturbance. Under the conditions in which the freezing tests are conducted in our laboratories, undercooling of water might be expected to be a rare occurrence. Actually, however, it is the rare occurrence when one or more of the cartons in which thermocouples are placed in a freezing load do not show undercooling.

In this particular part of the experimental work, there is no necessity for having the materials scrupulously clean. The thermocouples are either new, no attempt having been made to remove the soldering flux completely, or have been kept loose in a drawer since their previous use. More often than not, the cartons have been reparaffined one or more times if, in previous use, freezing cracked the seams. The water used is the ordinary distilled water of the laboratory, placed in the cartons the day before and allowed to stand uncovered at least 17 hours before the start of the test.

The test is begun at the start of an "on" period of a cycle. Hence, the cartons are subjected to continuous vibration if the compressor stays in operation until the end of the "freezing period," *i.e.* until the temperature in the last carton reaches 10° F. If the compressor cycles during that time, the cartons are subjected to the sudden jarrings at the start of the "on" periods and vibration during the running parts of the cycles.

The freezing compartment of the freezer being tested in the case discussed here was directly above the compressor, thus receiving the full impact of the starting of each period of operation. To check the magnitude of the agitation during the cycling of the compressor unit, at the conclusion of the test some uncovered cartons were distributed throughout a load in the freezing compartment. Standing waves of quite large amplitude were observed in each such carton, indicating that rather forceful disturbance was present while the compressor was in operation. During the test the compressor unit ran continuously for about 3 hours after the load was placed and then cycled approximately 260 times during the remaining 93 hours of the test. Some one or more of the cartons was in an undercooled state during 60 of these hours, during which time the compressor cycled 160 times. These figures do not support part of the quotation, viz., "The liquid at such a temperature is in a state of unstable equilibrium and will immediately solidify if disturbed. . . ."

Fig. 1 gives the temperature-time relationships in 6 of the 7 cartons in which temperatures were taken. Curve F is typical of those for a liquid passing through its solidification temperature without undercooling. Curves A and B are typical of the usual temperature-time relationships observed when undercooling does occur. Curves C, D, and E are seemingly atypical, but show the relationships when undercooling is prolonged.

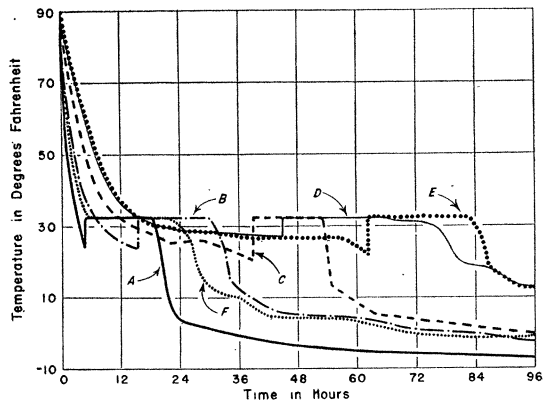

FIG. 1. Undercooling of water duiing home-freezer test.

Rapidity of cooling to and through 32° F. was not the deciding factor as to whether or not undercooling occurred. Curve A passes rapidly through the solidification temperature of 32° F., Curve E very slowly, and yet each exhibits undercooling. Curve F, representing a carton in which undercooling did not take place, came to the solidification temperature at a speed intermediate to these two. The temperature in the 7th carton (curve not shown) dropped to 32° F. more rapidly than any of the 6 for which curves are shown, and the water did not undercool.

An interesting feature shown by the graph is that, during the 9-hour period from 30 to 39 hours, the water in none of the cartons was at 32° F.; in three cartons the water had completely solidified, and in the other three it was in an undercooled state. Apparently the phenomenon of undercooling of water which is thought of as occurring only under nearly ideal conditions actually takes place under conditions far from ideal and does so to such an extent as to make questionable the accepted restrictions on the conditions required for its occurrence.

Reference

1. SMITH, A. W. *The elements of physics.* (4th ed.) New York-London: McGraw-Hill, 1938. P. 274.