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An Interesting Case of Undercooling

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"If a 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)

"Water can be cooled below 0°C. if kept quite undisturbed in a perfectly clean container. Other liquids and solutions can be similarly undercooled. But if an undercooled substance is jarred or disturbed by the addition of a small crystal of the solid, solidification proceeds rapidly, setting free heat that raises the temperature of the whole mass." (2)

Whenever the subject of undercooling of a liquid is taken up in a physics text, some such statements as those quoted appear in the discussion. The difficulties of getting a successful mass demonstration of the undercooling of water are well known. Hence it was thought worthwhile to report one of the interesting cases of water undercooling under what seem to be most unfavorable circumstances.

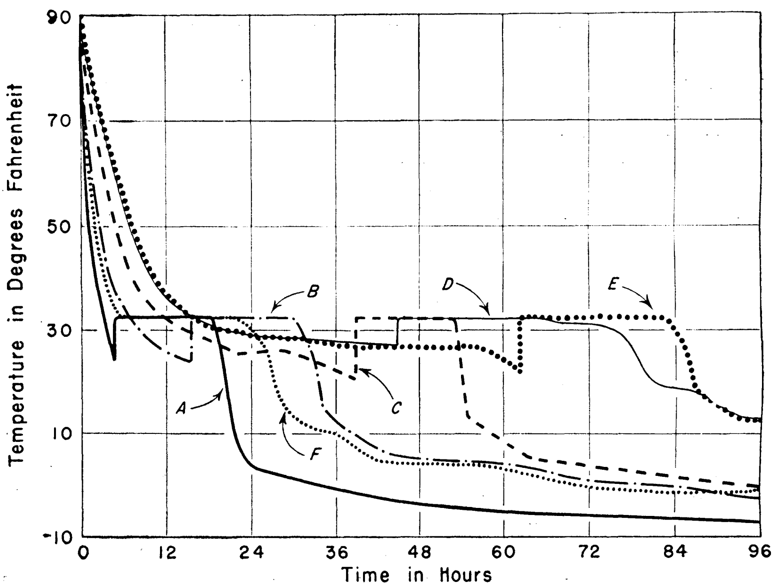
In carrying on investigations of the operating characteristics of home freezers in the United States Bureau of Human Nutrition and Home Economics, one of the tests includes the freezing of a volume-capacity load with water as the test material. The cartons used are pint, paraffined, nested, cardboard containers with disc lids. Copper-constantan thermocouples are used in connection with 16-point Brown Electronik temperature-recording potentiometers, each recording its series of 16 points in some few seconds less than one minute. Hence the temperatures at each location can be followed quite closely.

The procedure calls for temperatures to be taken in enough cartons in which water is being frozen to be sure that the temperatures are obtained in the cartons first and last to freeze. In the particular case described 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 occurred 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 disturbances. 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 thermocouples scrupulously clean. They are either newly made, with the soldering flux only poorly wiped from them, or they have been used in some other test and have been kept in a drawer. More often than not, the cartons used have been reparaffined from time to time as the freezing water has cracked their seams. The water used is the ordinary distilled water of the laboratory, placed in the cartons the day before and allowed to stand uncovered approximately 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 on until the end of the "freezing period", i.e., until the last carton reaches 10 F. If the compressor cycles during this time, the cartons are subjected to the sudden jarrings at the start of the "on" periods as well as to the vibration during the running parts of the cycles. The freezing compartment of a freezer is always located either at the adjacent side of or above the compressor unit so it receives the full impact of the starting of each period of operation. To determine the amount of agitation during the cycling of the compressor unit, uncovered cartons were placed in the freezing compartment of this freezer. Standing waves of quite large amplitude were observed in every carton. It was evident that rather forceful disturbance was present during the "on" parts of the cycles during the freezing period. In this experiment, 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 experiment. Some one carton or more was in an undercooled state 60 of these hours, during which time the compressor cycled



Graph 1. Undercooling of water in home freezer.

160 times. These figures seem to belie part of one of the quotations, viz., "The liquid at such a temperature is in a state of unstable equilibrium and will immediately solidify if disturbed. . ."

Graph 1 gives the temperature-time relationships in six of the seven 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 curves as obtained when undercooling does occur. Curves C, D and E are atypical and depict the relationships when the undercooling is prolonged. Rapidity of cooling to, and through, 32 F apparently is not the deciding factor as to whether or not undercooling will occur. Curve A gives the temperature-time relationships for a carton at the center of the bottom layer of the freezing compartment whose bottom liner is refrigerated; Curve E for a carton in the center of the top (fourth) layer just beneath the lid. The first one passed through the 32-degree temperature rapidly, the latter very slowly. Curve F, representing a carton in which the water did not undercool, came to the solidification temperature at a speed intermediate to these two. The temperature in the seventh carton (whose curve is not shown on the graph) dropped more rapidly than any of the others and the water did not undercool.

An interesting feature of the graph is that during the 9-hour period from 30 hours to 39 hours, the water in not one 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 which is thought of as occurring only under 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.

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