Freezing of Food Materials

Freezing is a unit operation that is intended to preserve foods without causing significant changes to their sensory qualities or nutritional value. It involves a reduction in the temperature of a food to below its freezing point, using either mechanical refrigeration or cryogens. It causes a proportion of the water in the food to undergo a change in state to form ice crystals. The immobilisation of water as ice and the resulting concentration of dissolved solutes in unfrozen water lower the water activity (a_w) of the food. The solutes form a glassy state, which acts as a cryoprotectant that reduces the damage to cellular tissues. This protects the texture of the food when the glass transition temperature is higher than the temperature of frozen storage. Preservation is achieved by a combination of low temperatures that reduce biochemical, enzymic and microbial activity, reduced water activity and, for vegetables, pretreatment by blanching. There are only small changes to nutritional value or sensory qualities of foods when correct freezing, storage and thawing procedures are followed. However, slow freezing, temperature abuse during frozen storage and thawing can each damage the quality of foods.

The main groups of commercially frozen foods are:

- Baked goods (e.g. bread, cakes, fruit and meat pies)
- Fish fillets and seafoods (e.g. cod, plaice, shrimps and crab meat) including fish fingers, fish cakes or prepared dishes with an accompanying sauce
- Fruits (e.g. strawberries, raspberries, blackcurrants) either whole or pureed, or as juice concentrates)
- Meats as carcasses, boxed joints or cubes, and meat products (e.g. sausages, beefburgers, reformed steaks)
- Prepared foods (e.g. pizzas, desserts, ice cream, ready meals and cook-freeze dishes)
- Vegetables (e.g. peas, green beans, sweetcorn, spinach, sprouts, potatoes).

Rapid increases in sales of frozen foods during the 1970s-1990s in industrialized countries were closely associated with increased ownership of domestic freezers and microwave ovens. Frozen foods are perceived by consumers as high quality and ‘fresh’ and, particularly in the meat, fruit and vegetable sectors, they outsell canned or dried products. However, distribution of frozen foods has a relatively high cost, due to the need to maintain a constant low temperature throughout the cold chain.

Theory

There are different stages involved in lowering the temperature of a food below its freezing point. First, sensible heat is removed and in fresh foods, heat produced by respiration is also removed. This is termed the ‘heat load’ and is important in determining the correct size of freezing equipment for a particular production rate. Next, latent heat is removed when water changes state to form ice. Most foods contain a large proportion of water, which has a high specific heat (4182 J kg^{-1} K^{-1}) and a high latent heat of crystallisation (334 kJ kg^{-1}). A substantial amount of energy is therefore needed to remove sensible and latent heat to form ice crystals. The latent heat of other components of the food (e.g. fats) must also be removed before they can solidify, but in most foods they are present in smaller amounts and require removal of a relatively small amount of heat for crystallisation to take place. Energy for freezing is supplied as electrical energy, which is used to compress refrigerants in mechanical freezing equipment or to compress cryogens.

Ice crystal formation

The initial freezing point of a food may be described as 'the temperature at which a minute crystal of ice exists in equilibrium with the surrounding water'. However, before an ice crystal can form, a nucleus of water molecules must be present. Nucleation therefore precedes ice crystal formation. There are two types of nucleation: homogeneous nucleation (the chance orientation and combination of water molecules), and heterogeneous nucleation (the formation of a nucleus around suspended particles or at a cell wall). Energetically it is easier for water molecules to migrate to existing nuclei in preference to forming new nuclei and heterogeneous nucleation is therefore more likely to occur in foods.

All food cells contain solutes such as carbohydrates, salts and other compounds that affect the way in which they freeze. In animal or vegetable tissues, water is both intracellular and extracellular; the extracellular fluids have a lower concentration of solutes and the first ice crystals are formed there. Higher rates of heat transfer produce larger numbers of nuclei and fast freezing therefore produces a large number of small ice crystals. This has beneficial effects in maintaining food quality. The time taken for the temperature of a food to pass through the 'critical zone' (Fig. 1), i.e. the freezing rate, therefore determines both the number and the size of ice crystals. However, large differences in crystal size are found with similar freezing rates due to differences in the composition of foods and even in similar foods that have received different prefreezing treatments.

Table 1. Water contents and freezing points of selected foods

Food	Water content (%)	Freezing point (°C)
Fruits	87–95	−0.9 to −2.7
Milk	87	−0.5
Vegetables	78–92	−0.8 to −2.8
Eggs	74	−0.5
Fish	65–81	−0.6 to −2.0
Meats	55–70	−1.7 to −2.2

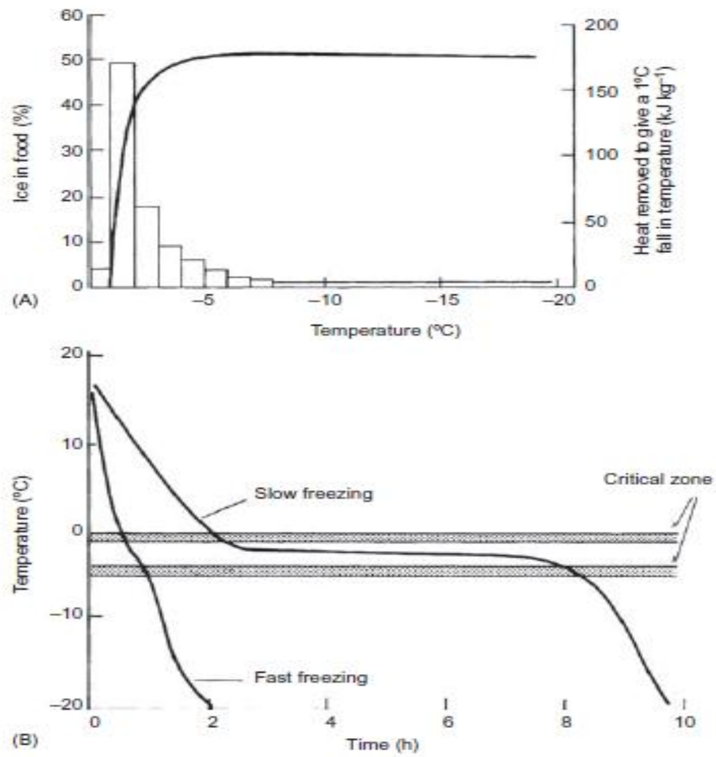

Figure 1. Freezing: (A) ice formation at different freezing temperatures and (B) temperature changes of food through the critical zone.

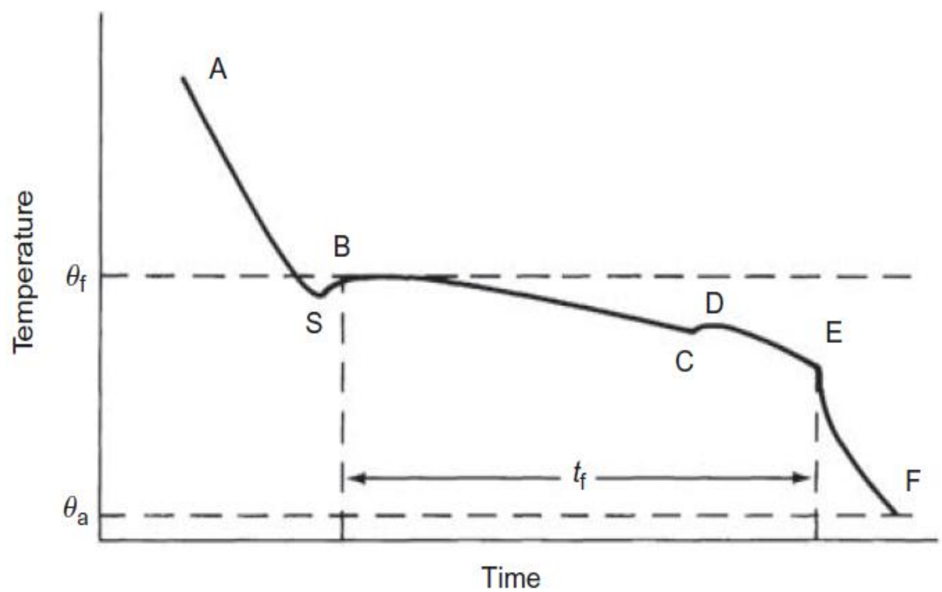

Figure 2. Time-temperature data during freezing.

If the temperature is monitored at the thermal centre of a food (the point that cools most slowly) as heat is removed, a characteristic curve is obtained (Fig. 2). The six components of the curve are as follows.

- A-S: The food is cooled to below its initial freezing point (θ_f) which, with the exception of pure water, is always below 0°C (Table 1). At point S, the water remains liquid, although the temperature is below the freezing point. This phenomenon is known as ‘supercooling’, which may be as much as 10°C below the freezing point, and is the period in which nucleation begins. The length of the supercooling period depends on the type of food and the rate at which heat is removed.
- S-B: The temperature rises rapidly to the freezing point as ice crystals begin to form and latent heat of crystallisation is released.
- B-C: Heat is removed from the food at the same rate as before, but it is latent heat being removed as ice forms and the temperature therefore remains almost constant at the freezing point. The freezing point is gradually depressed by the increase in solute concentration in the unfrozen liquor, and as more ice is formed the temperature falls slightly. Once stable nuclei are formed they continue to grow and it is during this stage that the major part of the ice is formed (Fig. 1A).
- C-D: One of the solutes becomes supersaturated and crystallises out. The latent heat of crystallisation is released and the temperature rises to the ‘eutectic’ temperature for that solute.
- D-E: Crystallisation of water and solutes continues. The total time (t_f) taken for ice crystal growth (the ‘freezing plateau’) depends on the rate of mass transfer of water from the liquid phase to the nuclei and the rate at which heat is removed. The temperature of the ice-water mixture falls to the temperature of the freezer. A proportion of the water remains unfrozen at the temperatures used in commercial freezing; the amount depends on the type and composition of the food and the temperature of storage. For example at a storage temperature of -20°C the percentage of water frozen is 88% in lamb, 91% in fish and 93% in egg albumin.
- E-F: If freezing is continued below commercial temperatures, ice formation and solute concentration continue until no more water can be frozen. The temperature falls as sensible heat is removed from the ice. The temperature (θ_a) at point F is known as the ‘glass transition temperature’ of the amorphous concentrated solution. When a critical, solute-dependent concentration is reached, the physical state of the unfrozen liquid changes from a viscoelastic liquid to a brittle, amorphous solid glass.

For the majority of the freezing plateau the rate of ice crystal growth is controlled by the rate of heat transfer. The rate of mass transfer (of water molecules moving to the growing crystal and of solutes moving away from the crystal) does not control the rate of crystal growth except towards the end of the freezing period when solutes become more concentrated.

Solute concentration

An increase in solute concentration during freezing causes changes to the pH, viscosity, surface tension and redox potential of the unfrozen liquor. As the temperature falls, individual solutes reach saturation point and crystallise out. The temperature at which a crystal of a solute exists in equilibrium with the unfrozen liquor and ice is its ‘eutectic’ temperature (e.g. for glucose it is -5°C, for sucrose: -14°C, for sodium chloride: -21.13°C and for calcium chloride: -55 °C). However, it is difficult to identify individual eutectic temperatures in the complex mixture of solutes in foods, and the term ‘final eutectic temperature’ is therefore used. This is the lowest eutectic temperature of the solutes in a food (e.g. for ice-cream it is -55°C, for meat: -50°C to -60°C and for bread: -70°C). Maximum ice crystal formation is not possible until this temperature is reached. Commercial foods are not frozen to such low temperatures and unfrozen water is therefore always present.

As food is frozen below point E in Fig. 2, the concentrated unfrozen material forms a ‘glass’ that encompasses the ice crystals. This can be represented on a simplified phase diagram for freezing of a solute in water (Fig 3) where:

- A-B: Cooling to the freezing point
- B-C: Supercooling
- C-D: Ice crystal growth
- D-E: The concentration of solutes in the unfrozen phase follows the solubility curve as it is cooled to the eutectic temperature (θ_e)
- E-F: The concentrated phase does not solidify at the eutectic temperature and cooling and concentration continue until the concentration meets the glass transition curve at temperature (θ_g).

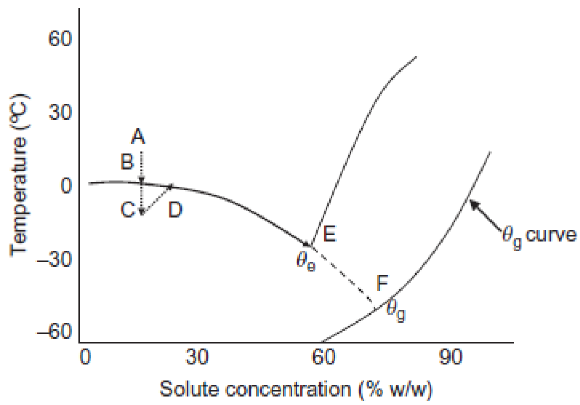

Figure 3. Simplified phase diagram showing the relationship between temperature and solute concentration down to glass transition temperature for a solute in water.

Glass transition temperatures for selected foods are shown in Table 2. Where the temperature of storage is below this temperature, the formation of a glass protects the texture of the food and gives good storage stability (e.g. meats and vegetables in Table 2). Many fruits, however, have very low glass transition temperatures and as a result suffer losses in texture during frozen storage in addition to damage caused by ice crystals.

Table 2. Glass transition temperatures for selected foods

Food	Glass transition temperature t_g (°C)
Dairy products	
Cheddar cheese	−24
Cream cheese	−33
Ice cream	−31 to −37
Ice milk	−30
Fish and meat	
Beef muscle	−12 to −60
Chicken	−16
Cod muscle	−11 to −77
Mackerel muscle	−12
Tuna muscle	−15 to −74
Fruits and fruit products	
Apple	−41 to −42
Apple juice	−40
Banana	−35
Grape juice	−42
Lemon juice	−43
Orange juice	−37.5
Peach	−36
Pear juice	−40
Pineapple juice	−37
Prune juice	−41
Strawberry	−33 to −41
Tomato	−33 to −41
Vegetables	
Broccoli, head	−12
Carrot	−26
Green beans	−27
Maize kernel	−15
Pea	−25
Potato	−12
Spinach	−17

Foods such as ice cream or surimi may be formulated to contain maltodextrin, sucrose or fructose, which raise the glass transition temperature, and if this is increased above the storage temperature, the shelf-life of the foods is extended.

In foods that contain a large proportion of water the formation of ice has a dramatic effect on their thermophysical properties:

- The density falls as the proportion of ice increases.
- The thermal conductivity increases (the thermal conductivity of ice is approximately four times greater than that of water.
- The enthalpy decreases

- The specific heat rises substantially as ice is formed and then falls back to approximately the same value as water when the temperature of the food is reduced to ~ -20°C
- The thermal diffusivity of the food increases after initial ice formation as the temperature is further reduced.

The changes to thermophysical properties mostly take place as the temperature of the food falls to ~ -10°C and then they change more gradually as the temperature falls further to that of frozen storage.

Calculation of the freezing point of foods, based on the Clausius-Clapeyron Equation and Raoult's Law, and methods to calculate the ice content of foods based on their thermophysical properties.