

# Freezing *(Ch. 21 of Fellows)*

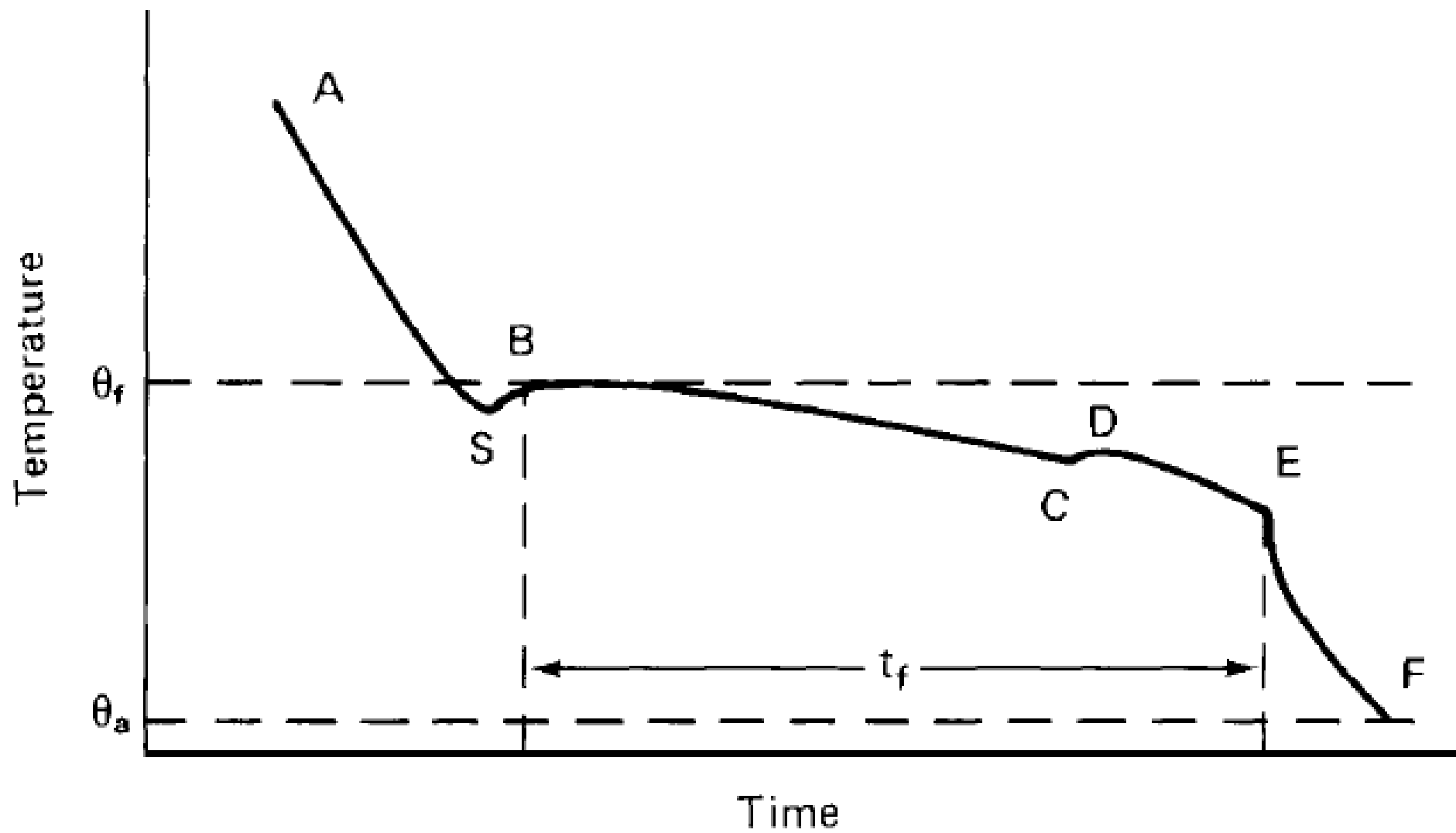
- Unit operation → temperature of a food is reduced below its freezing point & a proportion of the water undergoes a change in state to form ice crystals.
- The immobilisation of water to ice & resulting concentration of dissolved solutes in unfrozen water lower the  $A_w$  of the food
- Preservation → combination of low temperatures, reduced  $A_w$  &, in some foods, by blanching.
- Small changes to nutritional or sensory qualities of foods when correct freezing and storage procedures are followed.

- Major groups of commercially frozen foods:
  - fruits (strawberries, oranges, raspberries, blackcurrants), whole or pureed, or juice concentrates
  - vegetables (peas, green beans, sweetcorn, spinach, sprouts & potatoes)
  - fish fillets & seafoods (cod, plaice, shrimps and crab meat) incl. fish fingers, fish cakes or prepared dishes with sauce
  - meats (beef, lamb, poultry) as carcasses, boxed joints or cubes, & meat products (sausages, beefburgers, reformed steaks)
  - baked goods (bread, cakes, fruit & meat pies)
  - prepared foods (pizzas, desserts, ice cream, complete meals & cook–freeze dishes).

# *Theory*

- During freezing, sensible heat is 1<sup>st</sup> removed to lower the temperature of a food to the freezing point.
- In fresh foods, heat produced by respiration is also removed.  
: *heat load* → determining freezing equipment
- Most foods contain a large proportion of water, high specific heat ( $4200 \text{ J kg}^{-1}\text{K}^{-1}$ ) & high latent heat of crystallisation ( $335 \text{ kJ kg}^{-1}$ ).
- Substantial energy to remove latent heat, form ice crystals & freeze foods.
- Latent heat of other components of the food (e.g. fats) must be removed before they can solidify

- In most foods these components are present in smaller amounts & removal of a relatively small amount of heat is needed for crystallisation to take place.
- Energy for freezing → electrical energy to compress gases (refrigerants) in mechanical freezing equipment or to compress & cool cryogenes.



Time-temperature data during freezing.

### Water contents and freezing points of selected foods

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

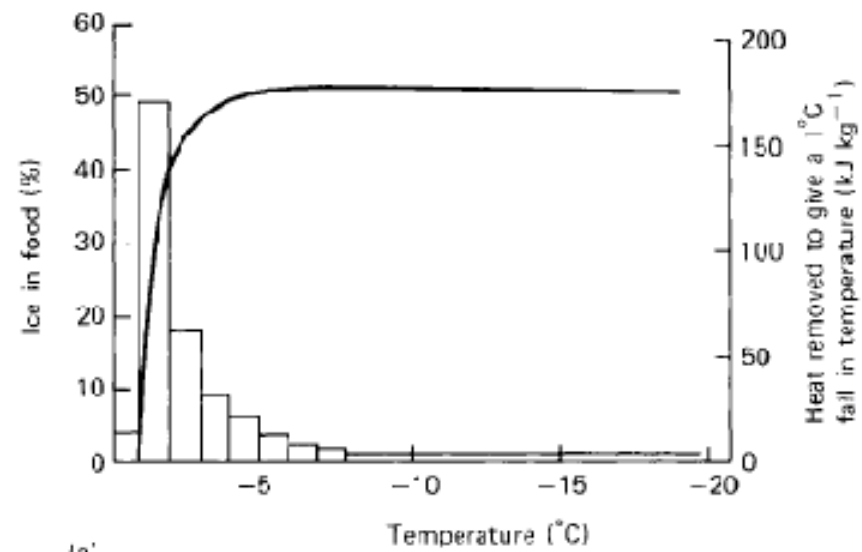
# ***Ice crystal formation***

- Freezing point of a food : ‘temperature at which a minute crystal of ice exists in equilibrium with the surrounding water’.
- Before an ice crystal can form, a nucleus of water molecules must be present.
- *Nucleation* precedes ice crystal formation.
- Two types of nucleation:
  - homogeneous nucleation (the chance orientation and combination of water molecules),
  - heterogeneous nucleation (the formation of a nucleus around suspended particles or at a cell wall).

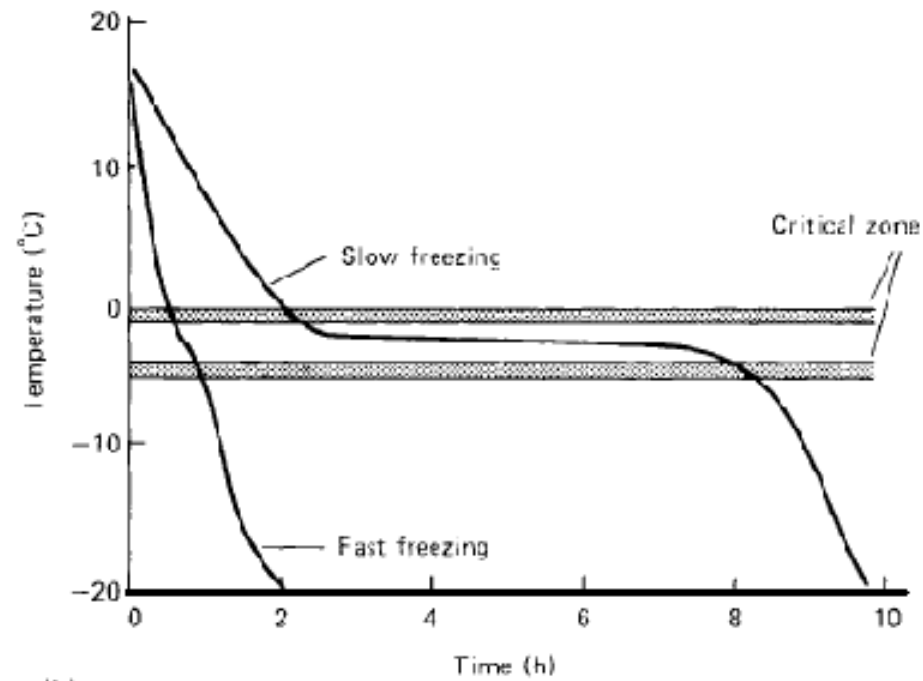
- Heterogeneous nucleation is more likely to occur in foods & takes place during super cooling.
- The length of super cooling period depends on type of food & rate at which heat is removed.
- High rates of heat transfer produce large numbers of nuclei
- As water molecules migrate to existing nuclei in preference to forming new nuclei, fast freezing produces a large number of small ice crystals.



- Large differences in crystal size with similar freezing rates due to different types of food & even in similar foods which have received different pre-freezing treatments.
- Rate of ice crystal growth is controlled by rate of heat transfer for the majority of the freezing plateau.
- Time for food temperature to pass through *critical zone*; determines number & size of ice crystals.
- Rate of mass transfer (of water molecules moving to growing crystal & of solutes moving away from crystal) does not control rate of crystal growth except towards the end of freezing period when solutes become more concentrated.



(a)



(b)

Freezing: (a) ice formation at different freezing temperatures; (b) temperature changes of food through the critical zone. (After Leriger and Beverloo (1975).)

# ***Solute concentration***

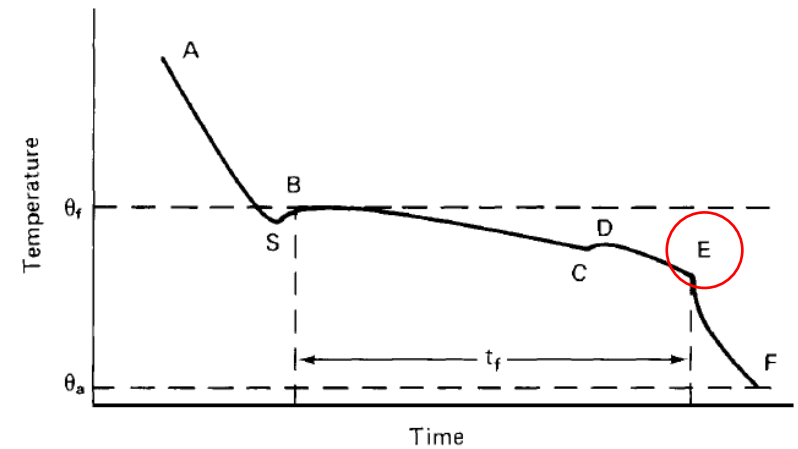
- Solute concentration increases during freezing  
→ changes in the pH, viscosity, surface tension & redox potential of the unfrozen liquor.
- As the temperature falls, individual solutes reach saturation point & crystallise out.
- Temperature at which a crystal of an individual solute exists in equilibrium with the unfrozen liquor & ice = its *eutectic temperature*  
E.g. for glucose  $-5^{\circ}\text{C}$ , for sucrose  $-14^{\circ}\text{C}$ , for NaCl  $-21.13^{\circ}\text{C}$  & for CaCl  $-55^{\circ}\text{C}$ .

- Difficult to identify individual eutectic temperatures in the complex mixture of solutes in foods
  - *final eutectic temperature*
  - the lowest eutectic temperature of solutes in a food (e.g. for ice-cream  $-55^{\circ}\text{C}$ , for meat  $-50$  to  $-60^{\circ}\text{C}$  and for bread  $-70^{\circ}\text{C}$ ).
- Maximum ice crystal formation is not possible until this temperature is reached.
- Commercial foods are not frozen to such low temperatures & unfrozen water is always present.

## Examples of glass transition values of foods

Food	Glass transition temperature (°C)
Fruits and fruit products	
Apple	-41 to -42
Banana	-35
Peach	-36
Strawberry	-33 to -41
Tomato	-41
Grape juice	-42
Pineapple juice	-37
Vegetables	
Sweetcorn, fresh	-15
Potato, fresh	-12
Pea, frozen	-25
Broccoli head, frozen	-12
Spinach, frozen	-17
Desserts	
Ice cream	-31 to -33
Cheese	
Cheddar	-24
Cream cheese	-33
Fish and meat	
Cod muscle	-11.7 ± 0.6
Mackerel muscle	-12.4 ± 0.2
Beef muscle	-12 ± 0.3

Adapted from Fennema (1996).



Time-temperature data during freezing.

- As food is frozen below point E the unfrozen material becomes more concentrated & forms a 'glass' which encompasses the ice crystals.
- Temperature range at which this occurs depends on solute composition & initial water content of food.
- Storage temperature is below this temperature range  
→ formation of a glass protects food texture & good storage stability (e.g. meats and vegetables).
- Many fruits have very low glass transition temperatures  
→ suffer losses in texture during frozen storage, in addition to damage caused by ice crystals.

# *Volume changes*

- Ice volume is 9% > pure water
- Degree of food expansion after freezing due to:
  - moisture content  
higher moisture contents produce greater changes in volume
  - cell arrangement  
plant materials have intercellular air spaces which absorb internal increases in volume without large changes in their overall size  
(e.g. whole strawberries increase in volume by 3.0%; coarsely ground strawberries increase by 8.2% when both are frozen to 20°C)

- concentrations of solutes  
high concentrations reduce freezing point & do not freeze – or expand – at commercial freezing temperatures
- freezer temperature  
determines amount of unfrozen water & degree of expansion
- crystallised components, incl. ice, fats & solutes,  
contract cooled → reduces the volume of the food.



- Rapid freezing causes food surface to form a crust & prevents further expansion.

→ causes internal stresses to build up in food

→ makes pieces more susceptible to cracking or shattering, esp. when they suffer impacts during passage through continuous freezers.

# ***Calculation of freezing time***

*subject for independent study*

- During freezing, heat is conducted from food interior to surface & is removed by freezing medium.
- Factors influencing rate of heat transfer:
  - thermal conductivity of food
  - area of food available for heat transfer
  - distance that heat must travel through the food (size of the pieces)
  - temperature difference between food & freezing medium
  - insulating effect of the boundary film of air surrounding food
  - packaging, if present.

## Approaches:

- The *effective freezing time*
  - measures time that food spends in a freezer
  - used to calculate throughput of a manufacturing process
  
- The *nominal freezing time*
  - used as an indicator of product damage
  - it takes no account of initial conditions or different rates of cooling at different points on the surface of food.

- Calculation of freezing time is complicated due to:
  - differences in initial temperature, size & shape of individual pieces of food
  - differences in freezing point & rate of ice crystal formation within different regions of a piece of food
  - changes in density, thermal conductivity, specific heat & thermal diffusivity with a reduction in temperature of food.

- Removal of latent heat complicates the unsteady-state heat transfer calculations
- Practical purposes → formulae developed by Plank.
- Assumptions:
  - freezing starts with all water in food unfrozen but at its freezing point, & loss of sensible heat is ignored
  - heat transfer takes place sufficiently slowly for steady-state conditions to operate

- the freezing front maintains a similar shape to that of food (e.g. in a rectangular block the freezing front remains rectangular)
- there is a single freezing point
- the density of food does not change
- thermal conductivity & specific heat of food are constant when unfrozen & change to a different constant value when food is frozen.

- Freezing time for cubes

$$t_f = \frac{\lambda \rho}{\theta_f - \theta_a} \left[ \frac{L}{6} \left( \frac{1}{h} + \frac{x}{k_1} \right) + \frac{L^2}{24k_2} \right]$$

- $t_f$  (s): freezing time,
- $L$  (m): length of the cube,
- $h$  ( $\text{Wm}^{-2}\text{K}^{-1}$ ): surface heat transfer coefficient,
- $\theta_f$  ( $^{\circ}\text{C}$ ): freezing point of the food,
- $\theta_a$  ( $^{\circ}\text{C}$ ): temperature of the freezing medium,
- $\lambda$  ( $\text{J kg}^{-1}$ ): latent heat of crystallisation,
- $\rho$  ( $\text{kg m}^{-3}$ ): density of the food,
- $x$  (m): thickness of the packaging,
- $k_1$  ( $\text{Wm}^{-1}\text{K}^{-1}$ ): thermal conductivity of the packaging,
- $k_2$  ( $\text{W m}^{-1}\text{K}^{-1}$ ): thermal conductivity of the frozen zone,
- 6 & 24: factors represent the shortest distance between centre & surface of food (2 & 8 for slab, 4 & 16 for cylinder, 6 & 24 for sphere).

- heat transfer coefficient:

$$h = \frac{L}{6} \left[ \frac{t_f(\theta_f - \theta_a)}{\lambda\rho} - \frac{Lx}{6k_1} - \frac{L^2}{24k_2} \right]$$

- Many assumptions  
→ small underestimation of freezing time compared with experimental data.



# ***Equipment***

- Selection of equipment considers:
  - rate of freezing required;
  - size, shape & packaging requirements of food;
  - batch or continuous operation,
  - scale of production,
  - range of products to be processed
  - capital & operating costs.

- Freezers:
  - mechanical refrigerators,  
evaporate & compress a refrigerant in a continuous cycle  
use cooled air, cooled liquid or cooled surfaces to remove heat from foods
  - cryogenic freezers,  
use solid or liquid carbon dioxide, liquid nitrogen (or liquid Freon) directly in contact with food.

- Freezer, based on rate of movement of the ice front:
  - *slow freezers & sharp freezers* ( $0.2 \text{ cm h}^{-1}$ )  
incl. still-air freezers and cold stores
  - *quick freezers* ( $0.5\text{--}3 \text{ cm h}^{-1}$ )  
incl. air-blast & plate freezers
  - *rapid freezers* ( $5\text{--}10 \text{ cm h}^{-1}$ )  
incl. fluidised-bed freezers
  - *ultrarapid freezers* ( $10\text{--}100 \text{ cm h}^{-1}$ ),  
cryogenic freezers.
- All freezers are insulated with expanded polystyrene, polyurethane or other materials which have low thermal conductivity

# ***Cooled-air freezers***

- ***Chest freezers***
- food is frozen in stationary (natural-circulation) air at between  $-20^{\circ}\text{C}$  &  $-30^{\circ}\text{C}$ .
- not used for commercial freezing due to low freezing rates (3–72 h)
  
- ***Cold stores***
- to freeze carcass meat, to store foods that are frozen by other methods, as hardening rooms for ice cream.
- Air is usually circulated by fans to improve the uniformity of temperature distribution, but heat transfer coefficients are low

## A comparison of freezing methods

Method of freezing	Typical film heat transfer coefficients ( $\text{W m}^{-2} \text{K}^{-1}$ )	Typical freezing times for specified foods to $-18^\circ\text{C}$ (min)	Food
Still air	6–9	180–4320	Meat carcass
Blast ( $5 \text{ m s}^{-1}$ )	25–30	15–20	Unpackaged peas
Blast ( $3 \text{ m s}^{-1}$ )	18	–	
Spiral belt	25	12–19	Hamburgers, fish fingers
Fluidised bed	90–140	3–4	Unpackaged peas
		15	Fish fingers
Plate	100	75	25 kg blocks of fish
		25	1 kg carton vegetables
Scraped surface	–	0.3–0.5	Ice cream (layer approximately 1 mm thick)
Immersion (Freon)	500	10–15	170 g card cans of orange juice
		0.5	Peas
		4–5	Beefburgers, fish fingers
Cryogenic (liquid nitrogen)	1500	1.5	454 g of bread
		0.9	454 g of cake
		2–5	Hamburgers, seafood
		0.5–6	Fruits and vegetables

Adapted from Earle (1983), Olsson and Bengtsson (1972), Desrosier and Desrosier (1978), Leeson (1987) and Holdsworth (1987).

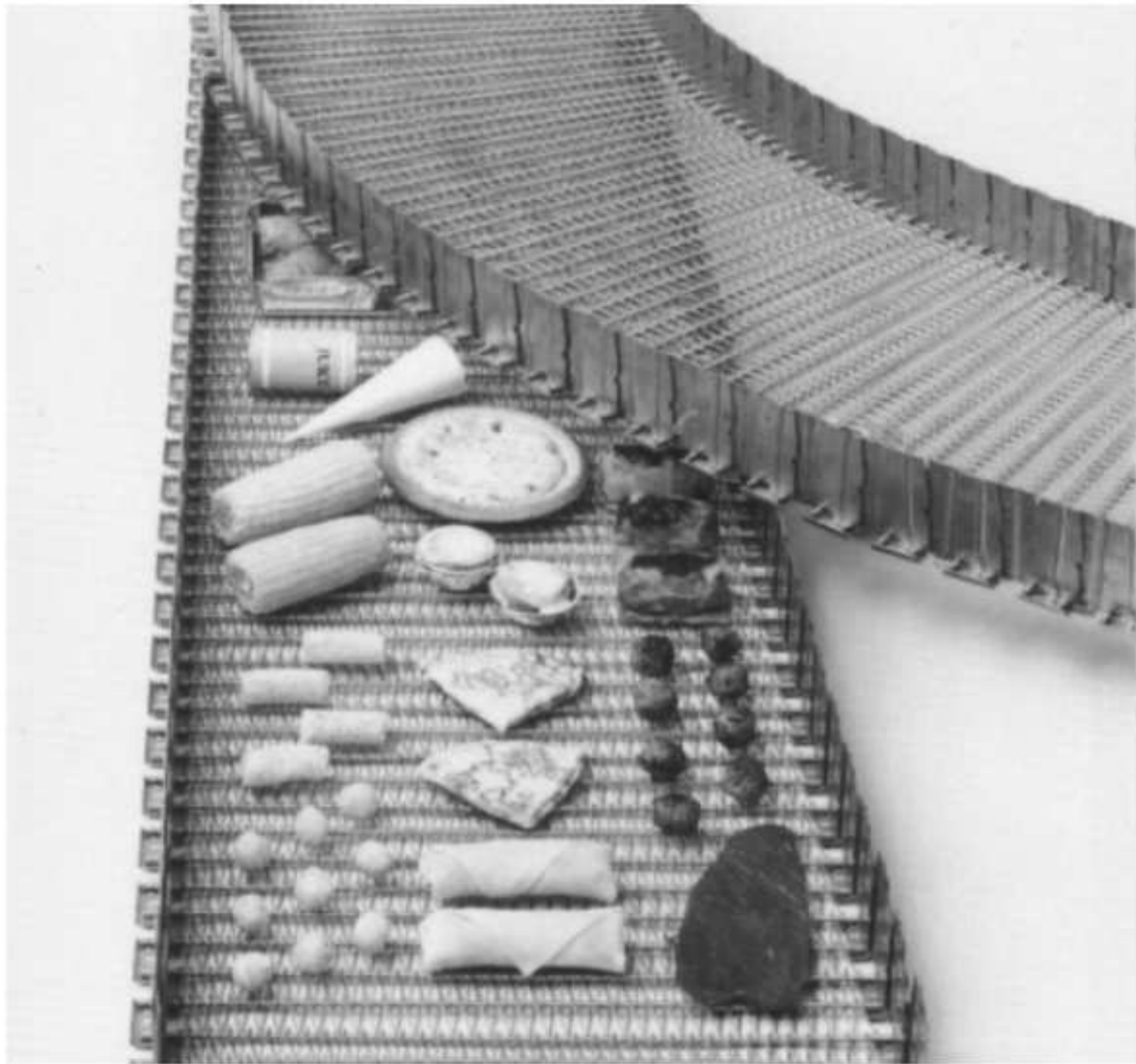
- Problem → ice formation on floors, walls & evaporator coils, caused by moisture from the air or from unpackaged products in the store.
- A desiccant dehumidifier overcomes these problems.
- ***Blast freezers,***
- air is re-circulated over food at between  $-30^{\circ}\text{C}$  &  $-40^{\circ}\text{C}$  at  $1.5\text{--}6.0\text{ m s}^{-1}$ .
- high air velocity reduces thickness of boundary films surrounding food → increases the surface heat transfer coefficient

- Batch equipment; food is stacked on trays in rooms or cabinets.
- Continuous equipment; consists of trolleys stacked with trays of food or on conveyor belts which carry the food through an insulated tunnel.
- Relatively economical & highly flexible; foods of different shapes & sizes can be frozen.

- Moisture from food is transferred to air & builds up as ice on refrigeration coils → frequent defrosting.
- Large volumes of recycled air can cause dehydration losses, freezer burn & oxidative changes to unpackaged or individually quick frozen (IQF) foods.
- IQF foods freeze more rapidly, enable packaged foods to be partly used & refrozen; better portion control.
- Low bulk density and high void space causes a higher risk of dehydration & freezer burn.



- ***Belt freezers (spiral freezers)***
- continuous flexible mesh belt formed into spiral tiers & carries food up through a refrigerated chamber.
- Cold air or sprays of liquid nitrogen are directed through the belt stack in a countercurrent flow → reduces weight losses due to evaporation of moisture.
- Spiral freezers require relatively small floor-space and have high capacity.
- Automatic loading & unloading, low maintenance costs & flexibility to freeze a wide range of foods incl. pizzas, cakes, pies, ice cream, whole fish & chicken portions.



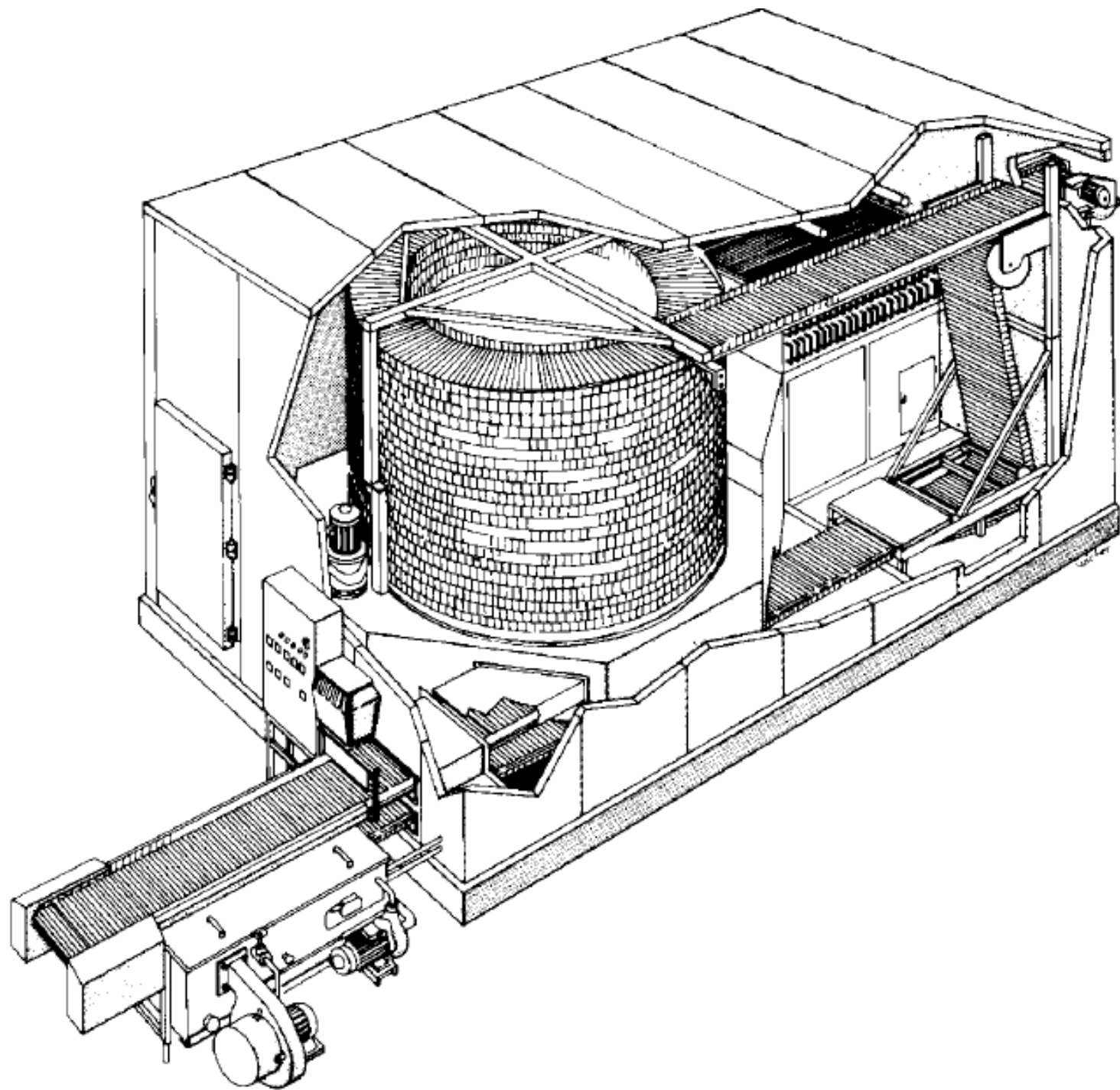
Spiral freezer, self-stacking belt.  
(Courtesy of Frigoscandia Ltd.)

- ***Fluidised-bed freezers***
- modified blast freezers in which air at between  $-25^{\circ}\text{C}$  and  $-35^{\circ}\text{C}$  is passed at  $2\text{--}6\text{ m s}^{-1}$  through a bed of food, contained on a perforated tray or conveyor belt.
- shape & size of pieces of food determine thickness of the fluidised bed & air velocity needed for fluidisation.
- Food comes into greater contact with air than in blast freezers, & all surfaces are frozen simultaneously & uniformly.
- higher heat transfer coefficients, shorter freezing times, higher production rates & less dehydration of unpackaged food than blast freezing.
- less frequent defrosting.

- restricted to particulate foods (e.g. peas, sweetcorn kernels, shrimps, strawberries or French fried potatoes).
- Similar equipment, = ***through-flow freezers***,
- air passes through a bed of food but fluidisation is not achieved,
- suitable for larger pieces of food (e.g fish fillets).
- Both types of equipment are compact, have a high capacity and are highly suited to IQF foods.

# ***Cooled-liquid freezers***

- ***immersion freezers***,
- packaged food is passed through a bath of refrigerated propylene glycol, brine, glycerol or  $\text{CaCl}_2$  solution on a submerged mesh conveyor.
- the liquid remains fluid throughout the freezing operation.
- high rates of heat transfer % capital costs low.
- commercially for concentrated orange juice in laminated card–polyethylene cans, & to pre-freeze film wrapped poultry before blast freezing.



# ***Cooled-surface freezers***

- ***Plate freezers***
- vertical or horizontal stack of hollow plates, through which refrigerant is pumped at  $-40^{\circ}\text{C}$ .
- batch, semi-continuous or continuous.
- Flat, relatively thin foods (e.g. filleted fish, fish fingers or beef burgers) placed in single layers between plates & a slight pressure is applied.
  - improves the contact between surfaces of food & plates
- If packaged food is frozen in this way, the pressure prevents the larger surfaces of the packs from bulging.

- Advantages:
  - good economy & space utilisation,
  - low operating costs compared with other methods,
  - little dehydration of the product & minimum defrosting of condensers,
  - high rates of heat transfer.
- Disadvantages
  - high capital costs,
  - restrictions on the shape of foods to those that are flat and relatively thin.



- ***Scraped-surface freezers***
- for liquid or semi-solid foods (e.g. ice cream).
- similar in design to evaporation & heat sterilisation but are refrigerated with ammonia, brine, or other refrigerants.
- In ice cream manufacture,
  - rotor scrapes frozen food from the wall of freezer barrel & simultaneously incorporates air.
  - Alternatively, air can be injected into the product.
  - The increase in volume of the product due to the air = *overrun*.

- Freezing is very fast; up to 50% of water is frozen within a few seconds
- results in very small ice crystals → smooth creamy consistency .
- temperature is reduced to between  $-4^{\circ}\text{C}$  and  $-7^{\circ}\text{C}$
- frozen aerated mixture is pumped into containers
- freezing is completed in a ‘hardening room’.

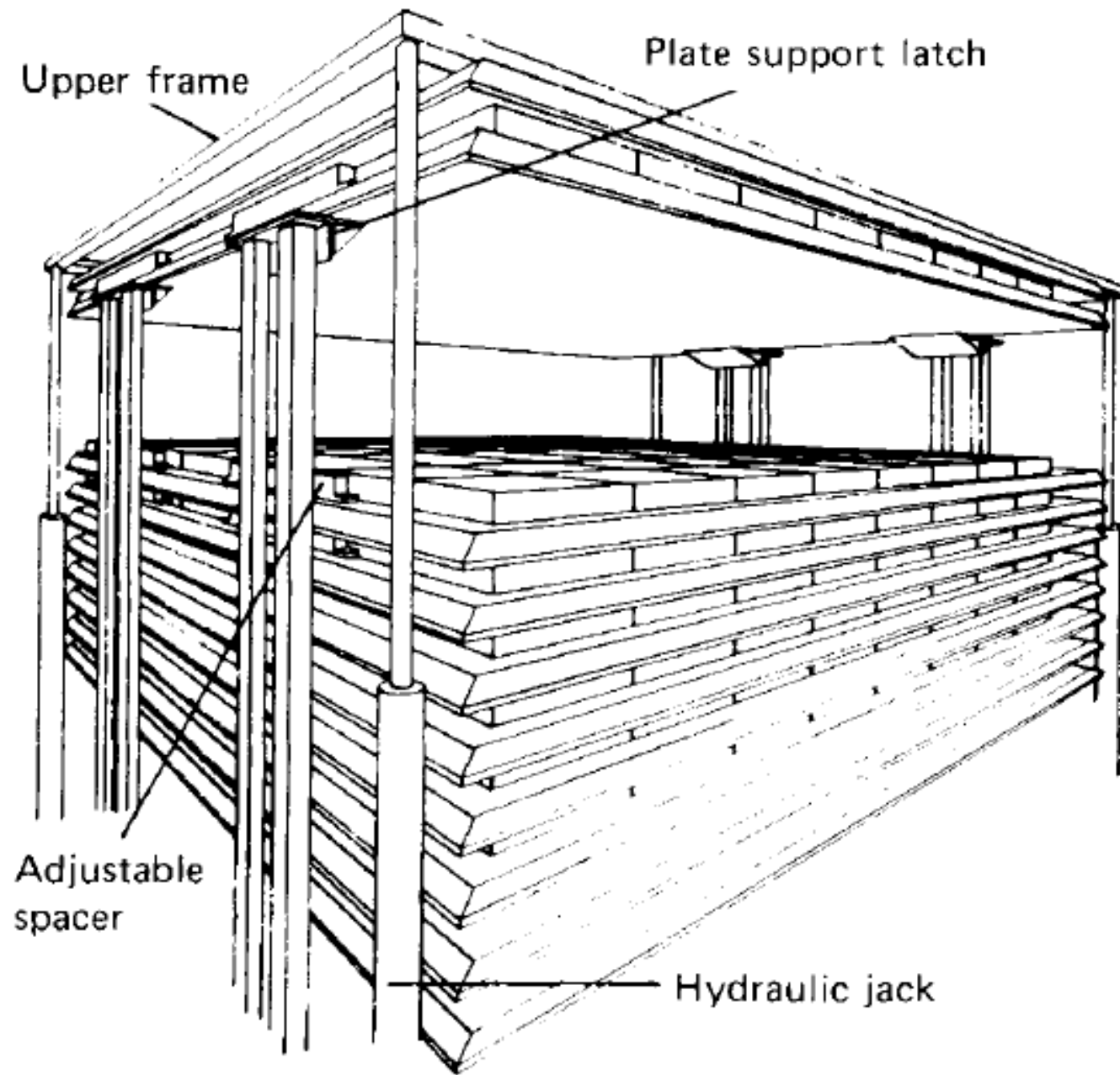


Plate freezer.

(Courtesy of Frigoscandia Ltd. and Garthwaite, A. (1995).)

# ***Cryogenic freezers***

- change of state in the refrigerant (or cryogen) as heat is absorbed from the freezing food.
- heat from food provides latent heat of vaporisation or sublimation of the cryogen.
- cryogen is in intimate contact with food & rapidly removes heat from all surfaces of the food to produce high heat transfer coefficients & rapid freezing.
- Refrigerants: liquid nitrogen & solid or liquid carbon dioxide.

- choice of refrigerant is determined by
  - technical performance for a particular product,
  - cost & availability,
  - environmental impact & safety.
- advantages
  - lower capital cost
  - flexibility to process different products without major changes to system.

- Liquid-nitrogen & carbon dioxide refrigerants are colourless, odourless & inert.
- When liquid nitrogen is sprayed onto food
  - 48% of total freezing capacity (enthalpy) is taken up by the latent heat of vaporisation needed to form the gas
  - 52% of the enthalpy is available in the cold gas
    - gas is recirculated to achieve optimum use of freezing capacity.

- Enthalpy of carbon dioxide < liquid nitrogen
- most of the freezing capacity (85%) is available from the subliming solid
- lower boiling point produces a less severe thermal shock.
- solid carbon dioxide in the form of a fine snow sublimes on contact with food, & gas is not recirculated.
- Carbon dioxide is a bacteriostat but toxic; gas should be vented from factory to avoid injury to operators.
- Consumption of carbon dioxide > liquid-nitrogen, but storage losses are lower.

Properties of food cryogens

Property	Liquid nitrogen	Carbon dioxide
Density ( $\text{kg m}^{-3}$ )	784	464
Specific heat ( $\text{kJ kg}^{-1} \text{K}^{-1}$ )	1.04	2.26
Latent heat ( $\text{kJ kg}^{-1}$ )	358	352
Total usable refrigeration effect ( $\text{kJ kg}^{-1}$ )	690	565
Boiling point ( $^{\circ}\text{C}$ )	-196	-78.5 (sublimation)
Thermal conductivity ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.29	0.19
Consumption per 100 kg of product frozen (kg)	100–300	120–375

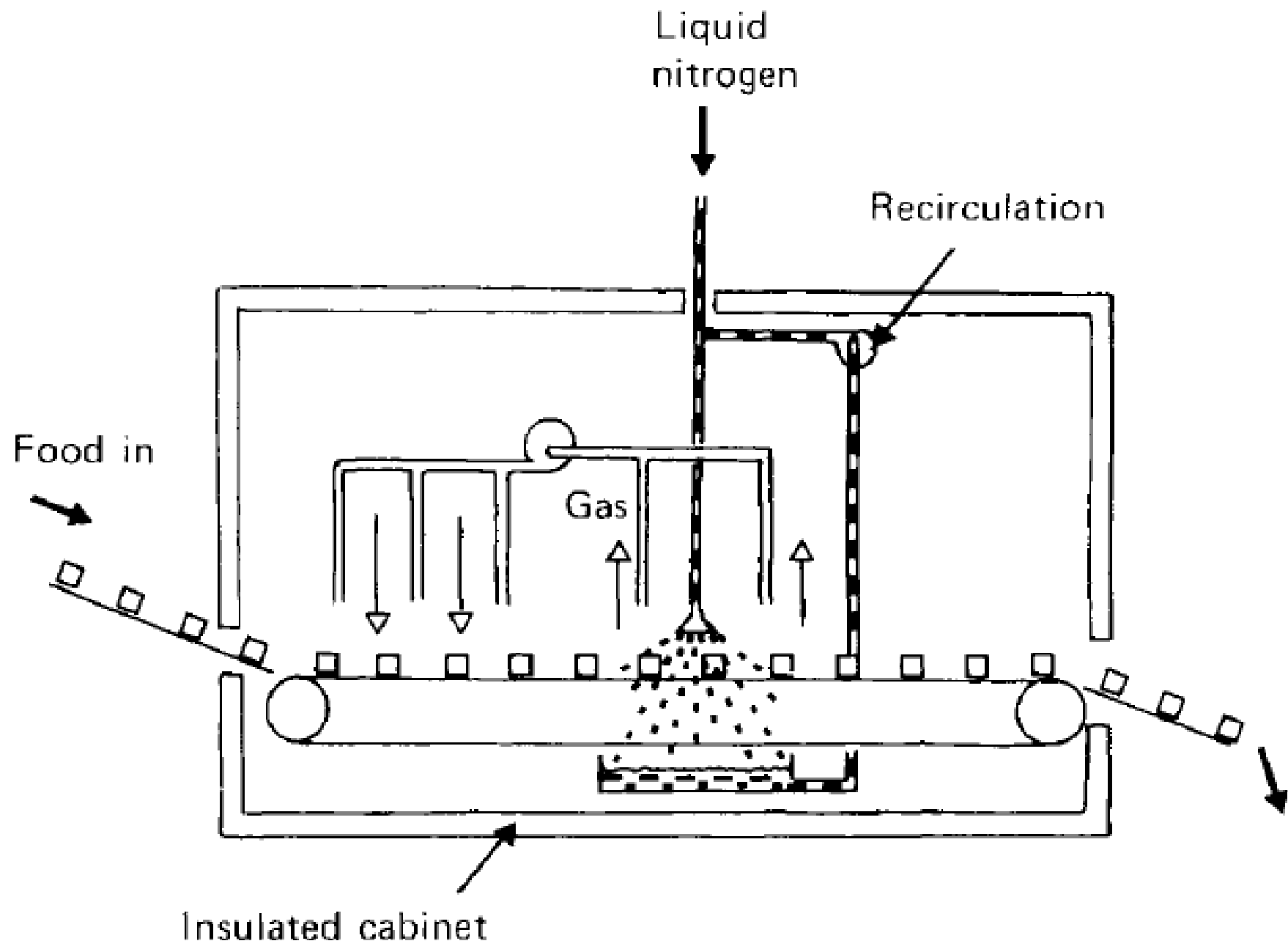
From Graham (1984).



- In liquid-nitrogen freezers, packaged or unpackaged food travels on a perforated belt through a tunnel
- it is frozen by liquid-nitrogen sprays and by gaseous nitrogen.
- temperature is allowed to equilibrate at the required storage temperature (between  $-18^{\circ}\text{C}$  &  $-30^{\circ}\text{C}$ ) before the food is removed from the freezer, or food is passed to a mechanical freezer to complete freezing process.
- use of gaseous nitrogen reduces thermal shock to food, & recirculation fans increase the rates of heat transfer.

- Other advantages:
  - simple continuous operation with relatively low capital costs
  - smaller weight losses from dehydration of the product
  - rapid freezing → smaller changes to sensory & nutritional characteristics of product
  - exclusion of oxygen during freezing
  - rapid startup & no defrost time
  - low power consumption.
- Main disadvantage is the relatively high cost of refrigerant (nitrogen & carbon dioxide consumption).

- Liquid nitrogen is also used in spiral freezers instead of vapour recompression refrigerators.
  - higher rates of freezing, smaller units for the same production rates because heat exchanger coils are not used.
- Other applications:
  - rigidification of meat for high-speed slicing,
  - surface hardening of ice cream prior to chocolate coating
  - crust formation on fragile products such as seafood & sliced mushrooms, before finishing freezing in mechanical or cryogenic freezers.
- Immersion of foods in liquid nitrogen produces no loss in product weight but causes a high thermal shock.
  - acceptable in some products (e.g. raspberries, shrimps & diced meat), but in many foods the internal stresses cause food to crack or split.



Liquid-nitrogen freezer.

# Changes in foods

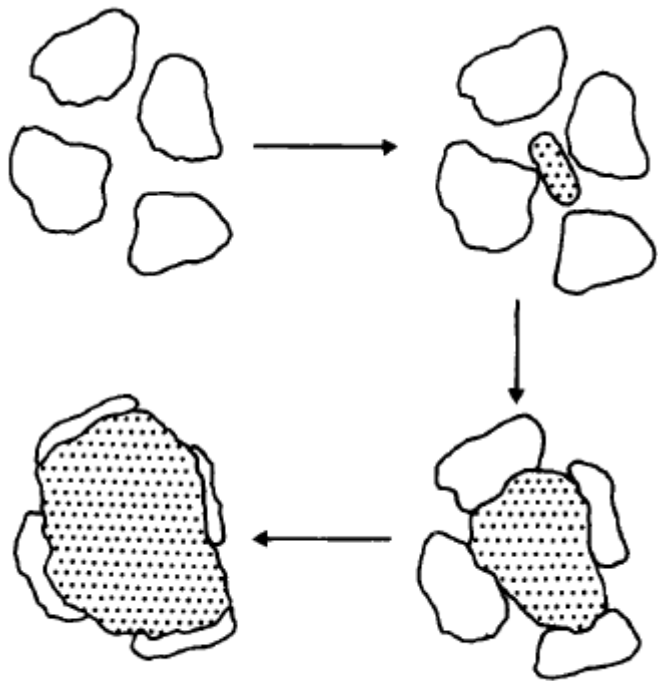
## *Effect of freezing*

- damage caused to cells by ice crystal growth.
- negligible changes to pigments, flavours or nutritionally important components, (these may be lost in preparation procedures or deteriorate later during frozen storage).
- food emulsions can be destabilised,
- proteins are sometimes precipitated from solution
- high proportion of amylopectin is needed in starch to prevent retrogradation & staling during slow freezing & frozen storage of baked goods.

- differences in resistance to freezing damage between animal & plant tissues.
  - Meats; more flexible fibrous structure which separates during freezing instead of breaking; texture is not seriously damaged.
  - Fruits & vegetables; more rigid cell structure may be damaged by ice crystals.
    - The extent of damage depends on size of crystals & on the rate of heat transfer.
- differences in variety & quality of raw materials & the degree of control over pre-freezing treatments have greater effect on food quality than changes caused by correctly operated freezing, frozen storage & thawing procedures.

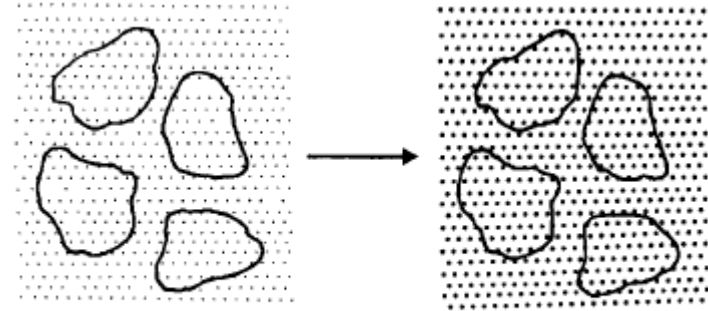
## Influence of freezing rate on plant tissues.

- During slow freezing, ice crystals grow in intercellular spaces  
→ deform & rupture adjacent cell walls.
- water vapour pressure of ice crystals < regions within the cells  
→ water moves from cells to growing crystals.



Effect of freezing on plant tissues: slow freezing.  
(After Meryman (1963).)

- Cells become dehydrated & permanently damaged by the increased solute concentration and a collapsed & deformed cell structure.
- On thawing, cells do not regain their original shape & turgidity.
- Food is softened & cellular material leaks out from ruptured cells ('drip loss').



Effect of freezing on plant tissues: fast freezing.

(After Meryman (1963))

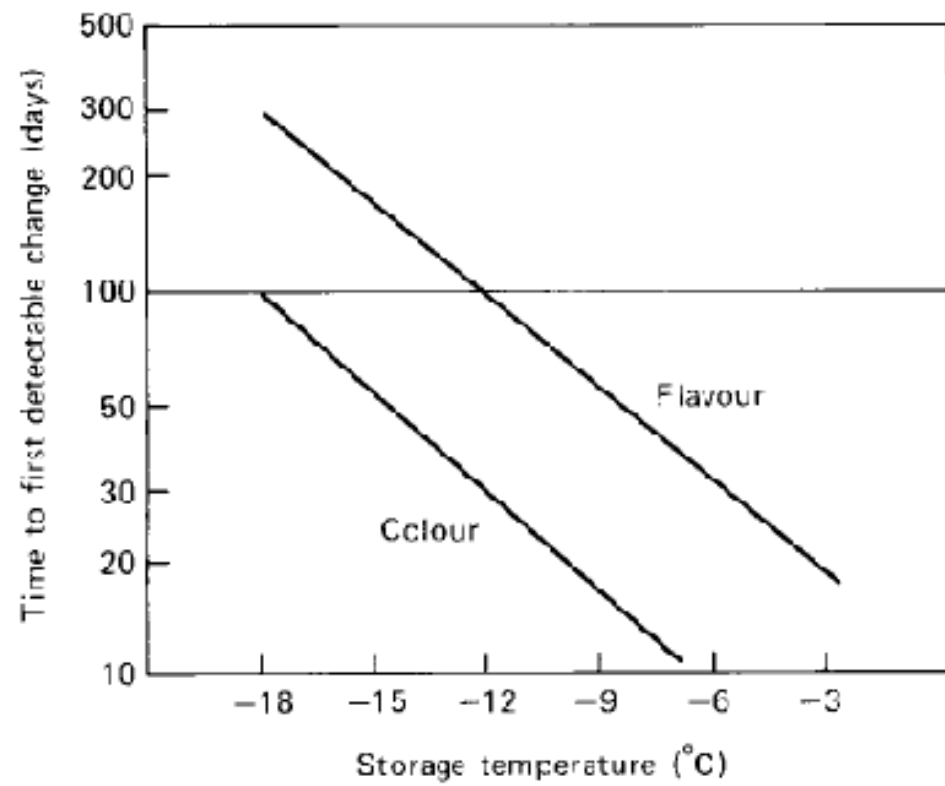
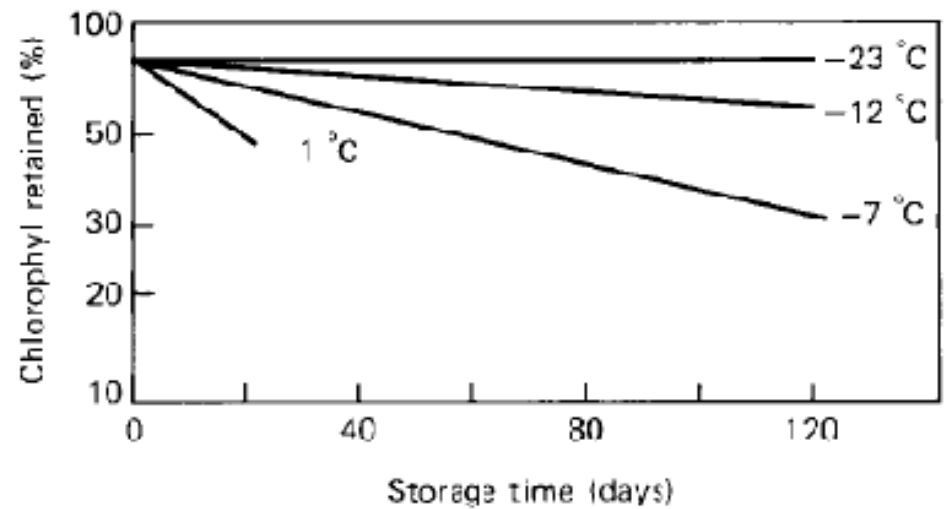
- In fast freezing, smaller ice crystals form within cells and intercellular spaces.
- little physical damage to cells; water vapour pressure gradients are not formed; minimal dehydration of the cells.
- texture of the food is retained.
- very high freezing rates may cause stresses within some foods → splitting or cracking of the tissues.



# ***Effects of frozen storage***

- the lower the temperature of frozen storage, the lower is the rate of microbiological & biochemical changes.
- not inactivate enzymes & have a variable effect on micro-organisms.
- lethal effect on micro-organisms of high storage temperatures (between  $-4^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ ) > lower temperatures (between  $-15^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$ ).
- Different types of micro-organism vary in resistance to low temperatures;  
vegetative cells of yeasts, moulds & gram negative bacteria (e.g. coliforms & *Salmonella* species) are most easily destroyed;

- Gram-positive bacteria (e.g. *Staphylococcus aureus* & *Enterococci*) & mould spores are more resistant,
- bacterial spores (especially *Bacillus* species & *Clostridium* species such as *C. botulinum*) are virtually unaffected by low temperatures.
- The majority of vegetables are blanched to inactivate enzymes & to reduce the numbers of contaminating micro-organisms.
- In fruits, enzyme activity is controlled by the exclusion of oxygen, acidification or treatment with sulphur dioxide.



Effect of storage temperature on sensory characteristics.  
(After Jul (1984).)

- At normal frozen storage temperatures ( $-18^{\circ}\text{C}$ ),
  - slow loss of quality (chemical changes & enzymic activity).
  - accelerated by high concentration of solutes surrounding the ice crystals, the reduction in water activity (to 0.82 at  $-20^{\circ}\text{C}$  in aqueous foods) and by changes in pH & redox potential.
- If enzymes are not inactivated, the disruption of cell membranes by ice crystals allows them to react to a greater extent with concentrated solutes.

Changes to frozen foods during storage:

- ***Degradation of pigments.***
- Chloroplasts & chromoplasts are broken down
- In fruits, changes in pH due to precipitation of salts in concentrated solutions change the colour of anthocyanins.
  
- ***Loss of vitamins.***
- Water-soluble vitamins are lost at sub-freezing temperatures.
- Vitamin C losses are highly temperature dependent; a 10°C increase in temperature causes a 6 to 20 x increase in the rate of vitamin C degradation in vegetables and a 30 to 70 x increase in fruits
- Losses of other vitamins are mainly due to drip losses, particularly in meat and fish (if the drip loss is not consumed).

- ***Residual enzyme activity.***
- inadequately blanched vegetables or fruits; polyphenoloxidase activity causes browning, lipoxygenases activity produces off-flavours & off-odours from lipids and causes degradation of carotene.
- Proteolytic & lipolytic activity in meats may alter the texture & flavour over long storage periods.
- ***Oxidation of lipids.***
- slowly at -18°C, causes off-odours & off-flavours.

## Vitamin losses during frozen storage

Product	Loss (%) at $-18^{\circ}\text{C}$ during storage for 12 months						
	Vitamin C	Vitamin B <sub>1</sub>	Vitamin B <sub>2</sub>	Niacin	Vitamin B <sub>6</sub>	Pantothenic acid	Carotene
Beans (green)	52	0-32	0	0	0-21	53	0-23
Peas	11	0-16	0-8	0-8	7	29	0-4
Beef steaks <sup>a</sup>		8	9	0	24	22	-
Pork chops <sup>a</sup>		+ - 18	0-37	+ - 5	0-8	18	-
Fruit <sup>b</sup>							
Mean	18	29	17	16	-	-	37
Range	0-50	0-66	0-67	0-33	-	-	0-78

+, apparent increase.

<sup>a</sup> Storage for 6 months.

<sup>b</sup> Mean results from apples, apricots, blueberries, cherries, orange juice concentrate (rediluted), peaches, raspberries and strawberries; storage time not given.

Adapted from Burger (1982) and Fennema (1975b).

## ***Recrystallisation***

- Physical changes to ice crystals (e.g. changes in shape, size or orientation): *recrystallisation*  
→ cause of quality loss in some foods.
- Types of recrystallisation in foods:
  1. *Isomass recrystallisation*.  
a change in surface shape or internal structure, usually resulting in a lower surface-area-to-volume ratio.
  2. *Accretive recrystallisation*.  
two adjacent ice crystals join together to form a larger crystal and cause an overall reduction in the number of crystals in the food.
  3. *Migratory recrystallisation*.  
an increase in the average size & a reduction in the average number of crystals, caused by the growth of larger crystals at the expense of smaller crystals.



- Migratory recrystallisation is the most important in most foods
  - caused by fluctuations in storage temperature.
- When heat is allowed to enter a freezer (e.g. by opening a door & allowing warm air to enter), the surface of food nearest to source of heat warms slightly.
  - ice crystals melt partially; the larger crystals become smaller & the smallest (less than 2  $\mu$ m) disappear.
  - melting crystals increase water vapour pressure
  - moisture moves to regions of lower vapour pressure.
  - areas of food nearest to heat source to dehydrate.
- When temperature falls again, water vapour does not form new nuclei but joins onto existing ice crystals
  - increasing their size.
- gradual reduction in the numbers of small crystals & an increase in the size of larger crystals, resulting in loss of quality similar to that observed in slow freezing.

- Cold stores have a low humidity because moisture is removed from air by refrigeration coils.
- Moisture leaves surface of food to storage atmosphere & produces areas of visible damage (*freezer burn*).
  - lighter colour due to microscopic cavities, previously occupied by ice crystals, which alter the wavelength of reflected light.
- Freezer burn is a particular problem in foods that have a large surface-area-to-volume ratio (e.g. IQF foods) but is minimised by packaging in moisture-proof materials.

- Temperature fluctuations are minimised by:
  - accurate control of storage temperature
  - automatic doors and airtight curtains for loading refrigerated trucks
  - rapid movement of foods between stores
  - correct stock rotation and control.
- These techniques + technical improvements in handling, storage and display equipment improved the quality of frozen foods.

- ***Storage life***
- European Community directive:  
frozen storage must 'preserve the intrinsic characteristics' of foods,
- the International Institute of Refrigeration:  
storage life is 'the physical and biochemical reactions . . . leading to a gradual, cumulative & irreversible reduction in product quality, such that after a period of time the product is no longer suitable for consumption . . .'
- Bogh-Sorensen:  
*practical storage life* (PSL) is 'the time the product can be stored and still be acceptable to the consumer'.

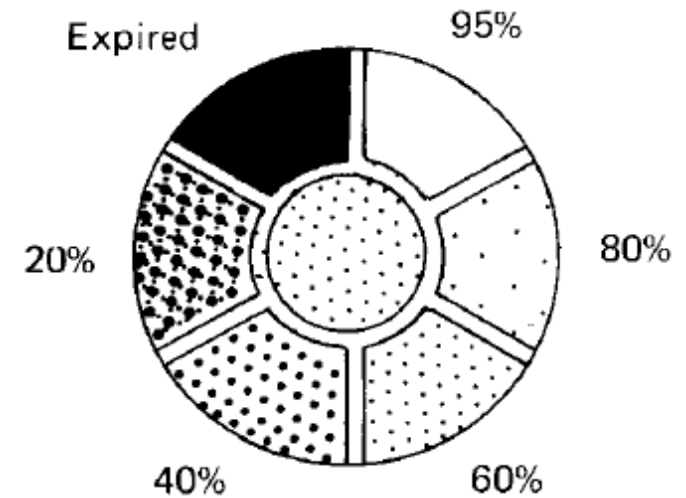
Storage life of meats measured by PSL and vegetables measured by HQL

Product	Practical storage life (PSL) (months)		
	-12°C	-18°C	-24°C
Beef carcasses	8	15	24
Ground beef	6	10	15
Veal carcasses	6	12	15
Lamb carcasses	18	24	>24
Pork carcasses	6	10	15
Sliced bacon	12	12	12
Chicken, whole	9	18	>24
Turkey, whole	8	15	>24
Ducks, geese, whole	6	12	18
Liver	4	12	18

High quality life (HQL) (months)

	-7°C	-12°C	-18°C
Green beans	1	3.1	9.8
Cauliflower	0.4	2	9.7
Peas	1	3	10.1
Spinach	0.76	1.9	6.2

From Guadagni (1968) and Evans and James (1993).

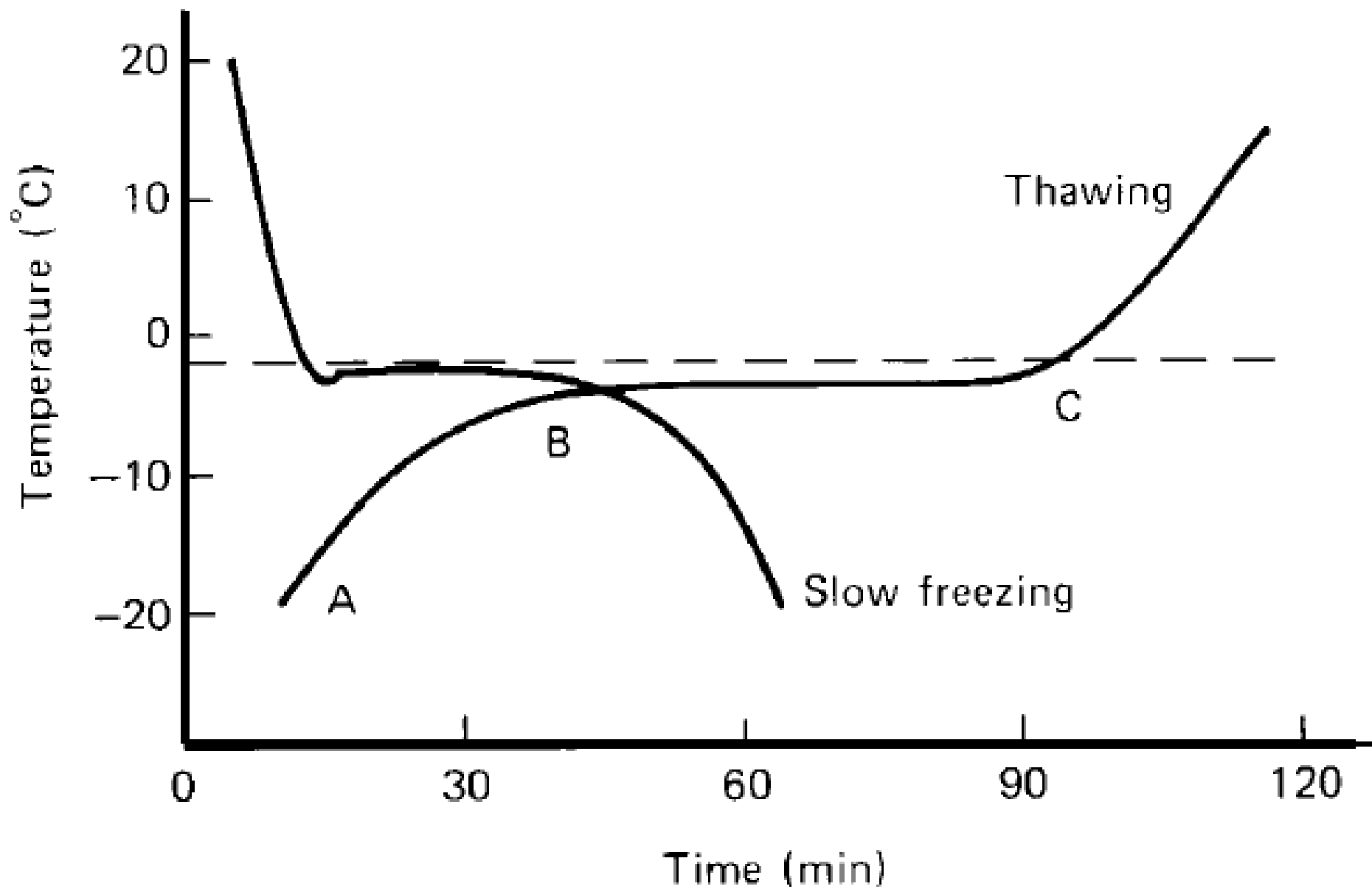


Time-temperature integrator.  
(After Fields and Prusik (1983).)

- loss of storage life
  - fluctuating temperatures
  - type of packaging used.
  - type of raw material,
  - pre-freezing treatments & processing conditions.
- Temperature fluctuation has a cumulative effect on food quality
- *Time-temperature tolerance* (TTT) and *product-processing-packaging* (PPP) concepts
  - monitor & control the effects of temperature fluctuations on frozen food quality during production, distribution and storage.

# *Thawing*

- When food is thawed in air or water, surface ice melts to form a layer of water.
- thermal conductivity & thermal diffusivity of water < ice; surface layer of water reduces the rate at which heat is conducted to the frozen interior.
- This insulating effect increases as the layer of thawed food grows thicker.
- During freezing, the increase in thickness of ice causes heat transfer to accelerate.
- Thawing is longer process than freezing when temperature differences and other conditions are similar.



Temperature changes during thawing.  
 (After Fennema and Powrie (1964).)



- Drip losses form substrates for enzyme activity & microbial growth.
- In the home, food is often thawed using a small temperature difference (e.g. 25–40°C, compared with 50–80°C for commercial thawing).
- This extends thawing period & increases the risk of contamination
- Commercially, foods are often thawed to just below the freezing point, to retain a firm texture for subsequent processing.
- Some foods are cooked immediately and are heated rapidly to a temperature which is sufficient to destroy micro-organisms.
- Others (e.g. ice cream, cream and frozen cakes) are not cooked and should be consumed within a short time of thawing.

- When food is thawed by microwave or dielectric heaters, heat is generated within the food, and the changes described above do not take place.
- The main considerations in thawing:
  - to avoid overheating
  - to minimise thawing times
  - to avoid excessive dehydration of the food.
- Commercially, foods are thawed in a vacuum chamber by condensing steam, at low temperatures by warm water (appr. 20°C) or by moist air which is re-circulated over the food.

Thank you