FREEZING

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History of freezing

HISTORY OF CHILLING AND FREEZING (CONTD)

DATE	*EVENT*
1930	BIRDSEYE INVENTS PLATE FREEZER
1960	IQF/ FLUIDISED BED
1961	CRYOGENIC FREEZING
1970'S	FAST FOOD TAKES OFF SUPERMARKET DELI COUNTERS
1980'S	MICROWAVEABLE FOODS
1990'S	HMR'S AND CAFÉ SOCIETY

What is freezing ?

A method of food preservation whereby:

- the heat is removed (heat of fusion)
- temperature of the food is reduced below its freezing point ($T<T_f$)
- and a portion of water in food undergoes a change in state to form ice crystals (A_w lowered)

Preservation by Freezing

Preservation achieved by:

- Low temperature
- Reduced water activity due to ice formation & high concentration of solutes in unfrozen water
- Blanching of some foods

Goal of freezing

- To prevent growth of microorganisms by
  - Killing some bacteria (little effect)
  - Reducing water activity
  - Mechanical formation of ice crystals
  - Osmotic changes in cell fluids
  - Tying up some free water
- To lower temperature enough to slow down chemical reactions
  - (every 10°C decrease in temperature halves the reaction rate)

FREEZING THEORY

General definitions

- Energy
  - Ability to work
- Heat
  - Energy in transit (dynamic) due to the temperature difference between the source and the product

- Specific heat
  - Is the quantity of heat that is gained or lost by a unit mass of products to a accomplish a unit change in temperature without the change in state (kJ/kg C)
- Sensible heat
  - Is that heat when added or subtracted from material changes their temperature and it can be sensed
- Latent heat
  - Is the heat required to change the physical state of materials at constant temperature

Freezing

What is the basis for freezing foods?

WATER

WATER CONTENT OF FOODS

Food	Water content(%)	Freezing Point (ºC)
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

Water

- When Water is chilled it reaches its max density at 4°C (Sg = 1) and freezes at 0°C (Sg = 0.917). That is why the ice floats in water

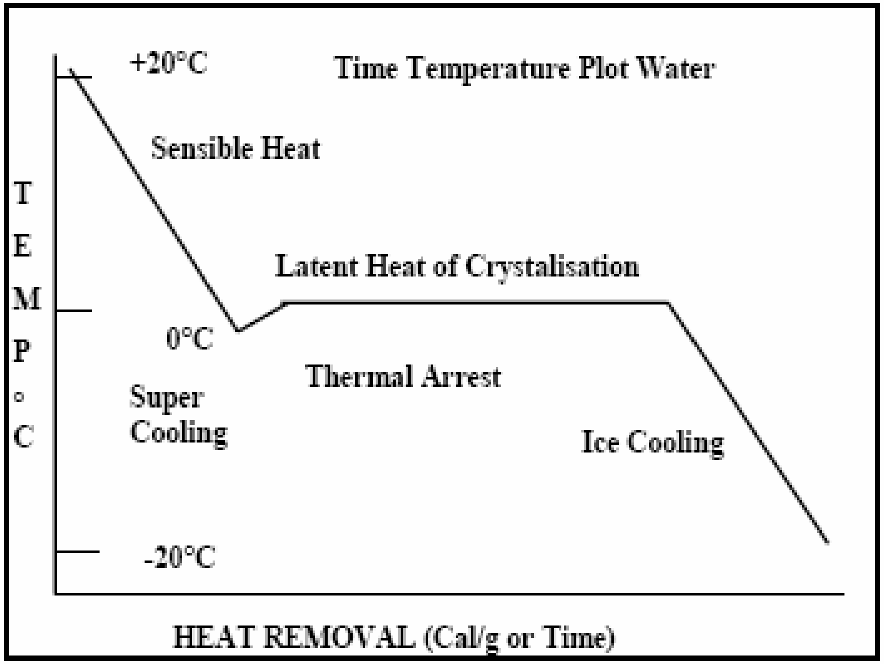
Food composition

- *Question:* WHAT ARE FOODS MADE OF?
- *Answer:* WATER+CHEMICALS
- Proteins
- Fats
- Carbohydrates
- Minerals
- Vitamins
- Enzymes
- **Water may be free or bound to other components in the food.**
- All water in foods does not freeze
- Frozen water @-20ºC
- Lamb=88%
- Fish=91%
- Egg=93%

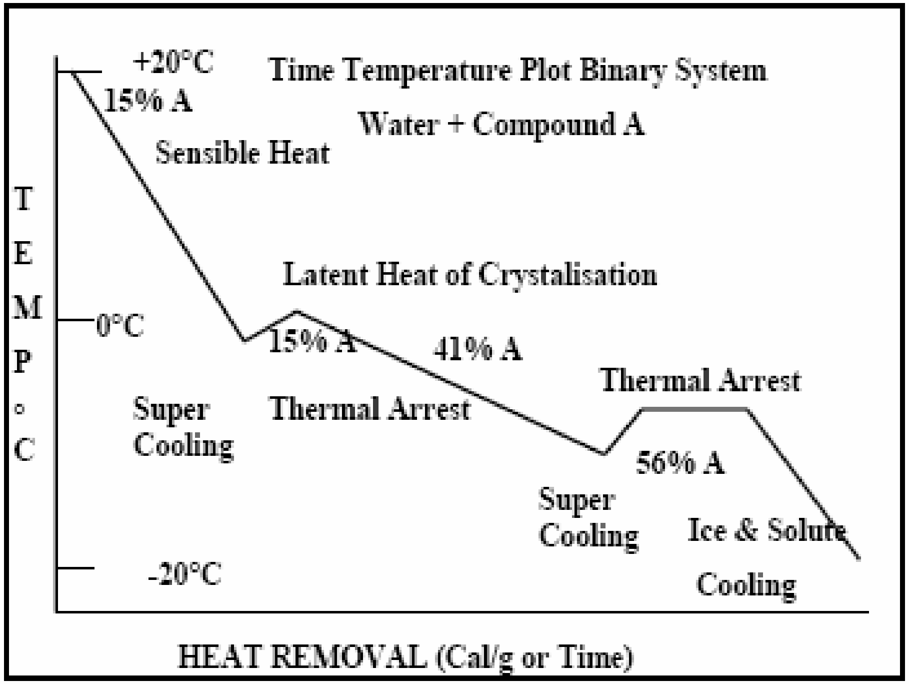
- Although food mostly consists of water, it contains lots of soluble materials
- Soluble materials slow down the movement of water molecules, and the freezing occurs at lower temperature
- 1gmol of soluble matter will decrease (lower) the freezing point by 1.86F (~1C).
- Freezing points:

Fruits and vegetables	29-30 F
Meat and fish	27-28 F

Freezing Curves for:
A- water, B- Binary system



A- water



B- Binary system

FREEZING a BINARY SYSTEM (notes on curve)

Cooling of water and component A

Super-cooling until nucleation

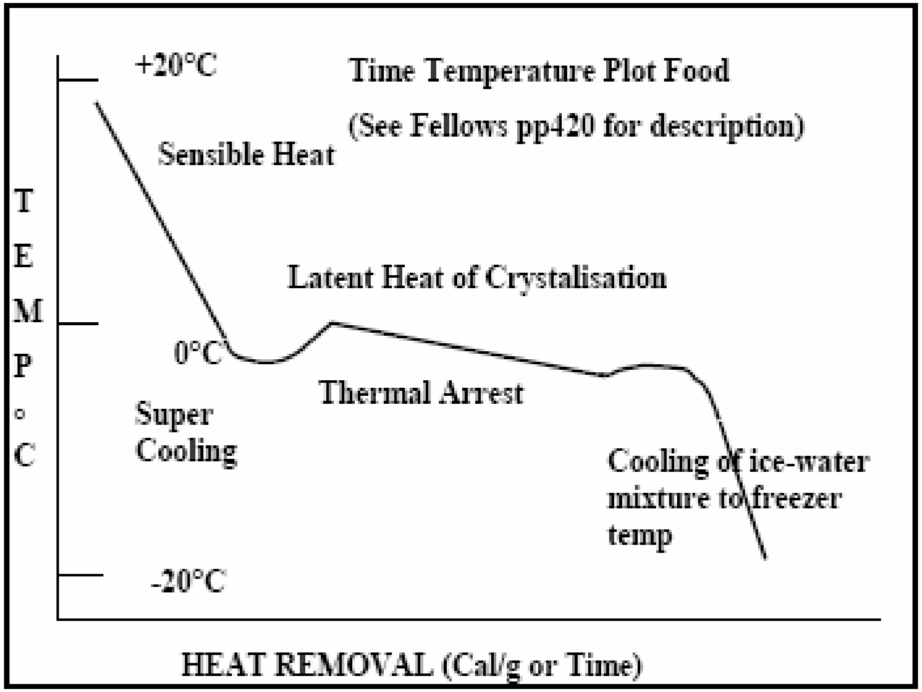
Release of latent heat of crystalisation

Freezing point depression as water freezes and concentration of component A increase

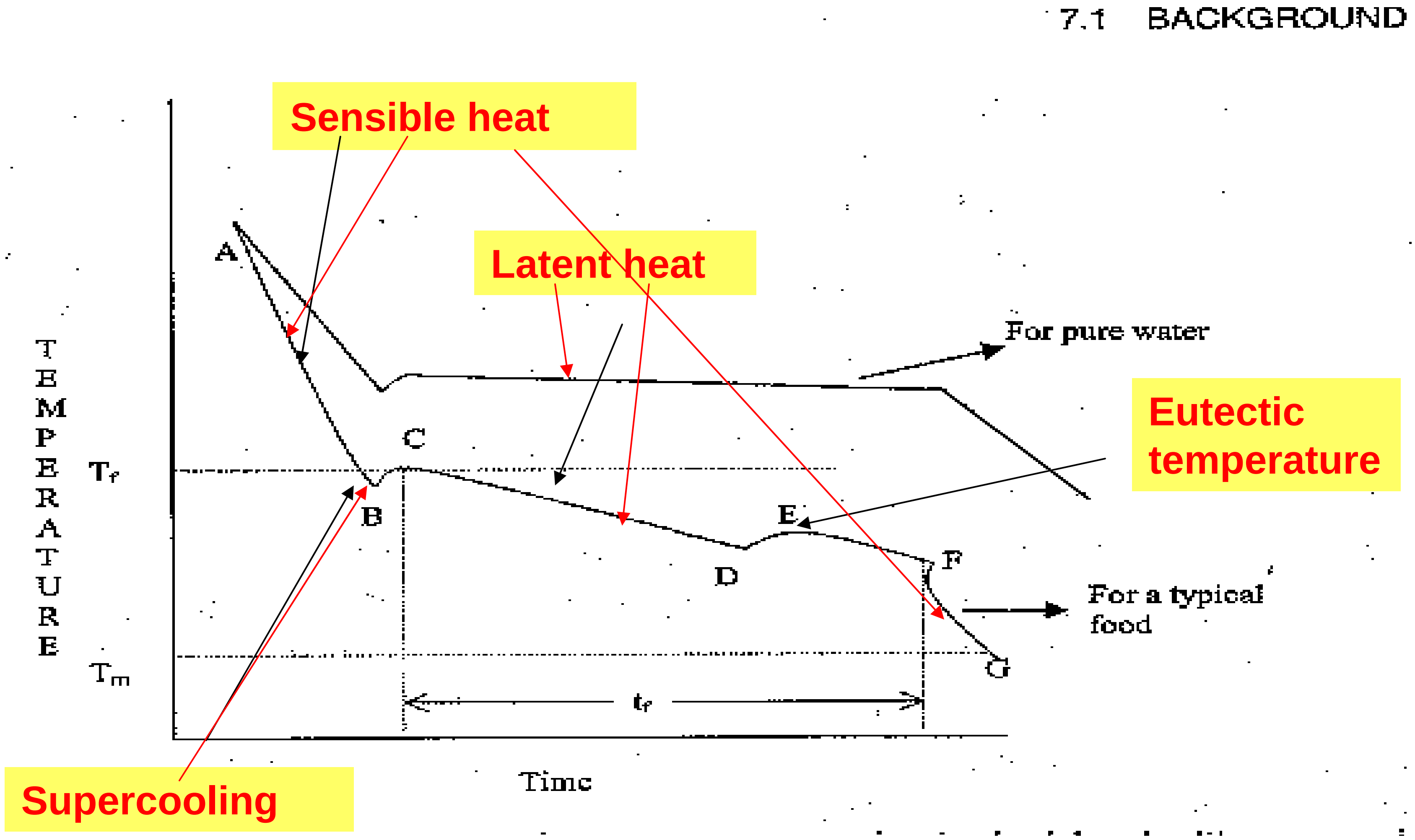
Component A crystalises out

Freezing of remaining water

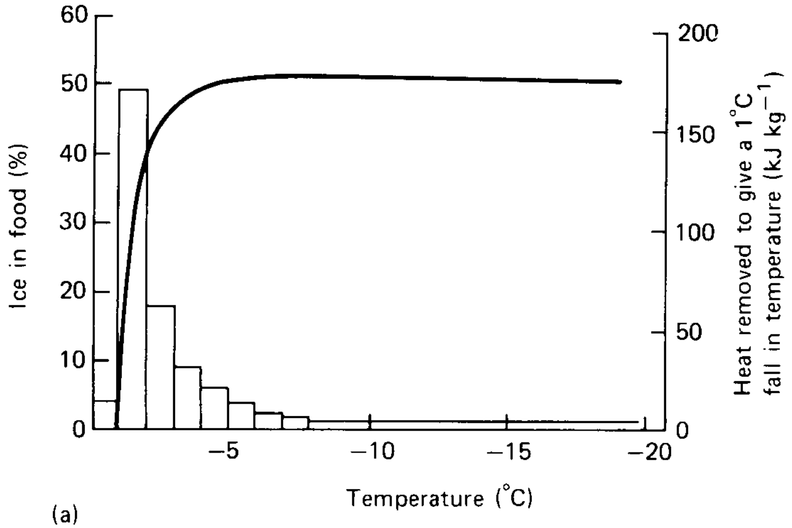
Cooling of Ice and component A to temp of freezing medium

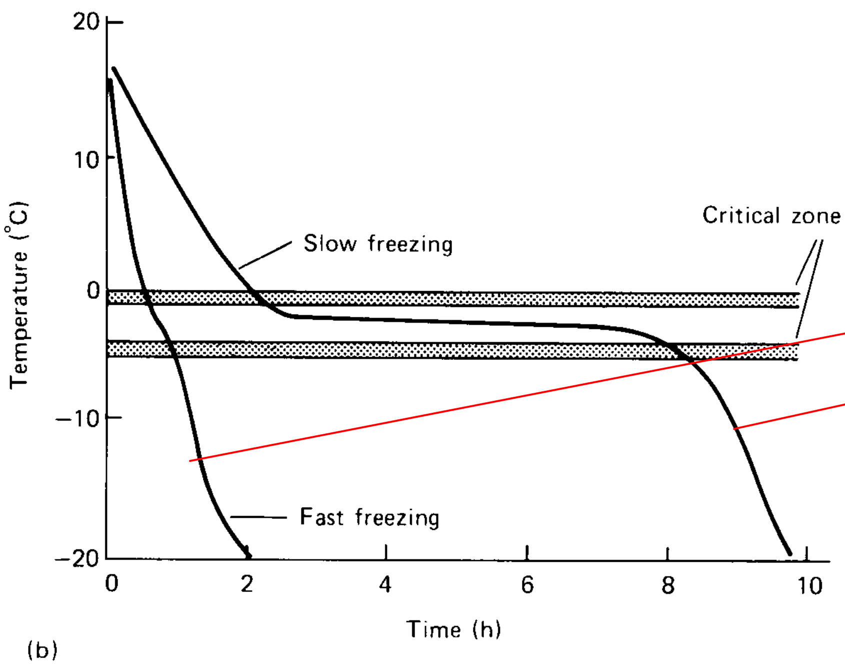


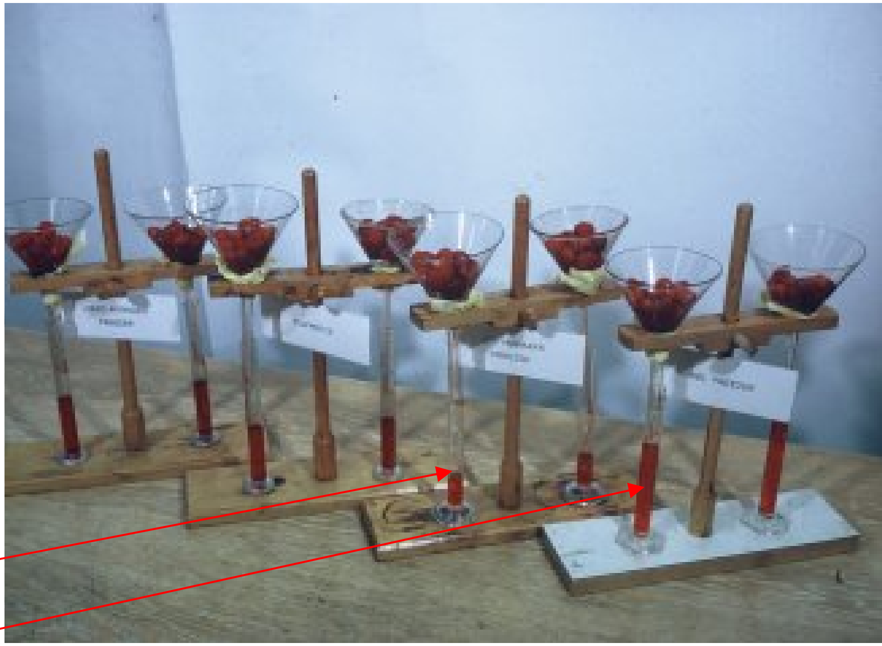
Freezing curve



Freezing curves (rates) and ice crystals







Frigoscandia Distribution

Freezing curve

- Point AB
  - Food cooled below freezing point (less than 0)
  - At point B water remains liquid although the temperature is below 0°C.
  - This phenomenon is called

SUPERCOOLING

Supercooling

- Going below freezing point without the formation of ice crystals (crystallization)

- It yields better quality food than if not present

- This shows that the undesirable effects of freezing are due to ice formation rather than reduction of temperature

Freezing curve

- Point **BC**
  - Temperature rises rapidly to the freezing point (giving off heat of fusion)
  - Ice crystals begin to form
  - Latent heat of crystallization is released

Ice crystals forming- Crystallization

- Consists of
  1. Nucleation (site for crystal formation and growth)
     - Association of molecules into a tiny ordered particles sufficient to survive and serve as a site for crystal growth. It can be:
       - Homogenous (pure water)
       - Heterogeneous (most foods)
       - Dynamic (spontaneous)
  2. Crystal growth (where it is formed)
     - Is the enlargement of the nucleus by the orderly addition of molecules. Crystal growth can occur at temperatures just below melting point while nucleation starts at lower temperature (supercooling)
     - Heat transfer is most responsible for limiting the rate of crystallization due to the large amount of latent heat needed

Ice crystal growth

THE FREEZING PROCESS

2 Ice Crystal Growth

Water in cell has lower F Pt due to dissolved solutes

Water in cellular spaces will freeze first

Water vapour moves from inside cell to cellular spaces because of VP difference

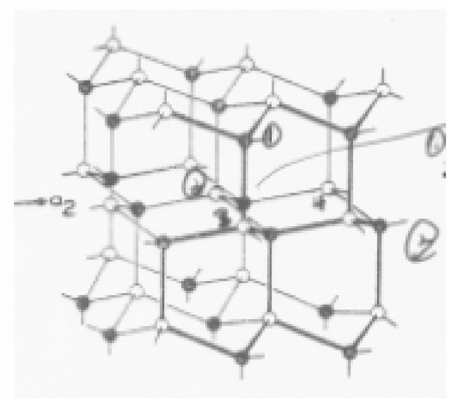
Inter-cellular ice crystals grow

Rate & size governed by freezing rate

Slow Freezing ⟶ Large Inter cellular Xtals

Fast Freezing ⟶ Small Inter cellular Xtals

3D (Hexagonal) Structure of Water



● - Oxygen o - Hydrogen

Freezing curve

- Point CD
  - Heat is removed as latent heat so the T=constant
  - Major part of ice is formed
  - In unfrozen liquid there is an increase in solute concentration and that is why the temperature falls slightly

Freezing curve

- Point DE
  - One of the solutes becomes supersaturated and crystallizes out.
  - Latent heat of crystallization is realized and the temperature rises to EUTECTIC point for that solute

EUTECTIC POINT

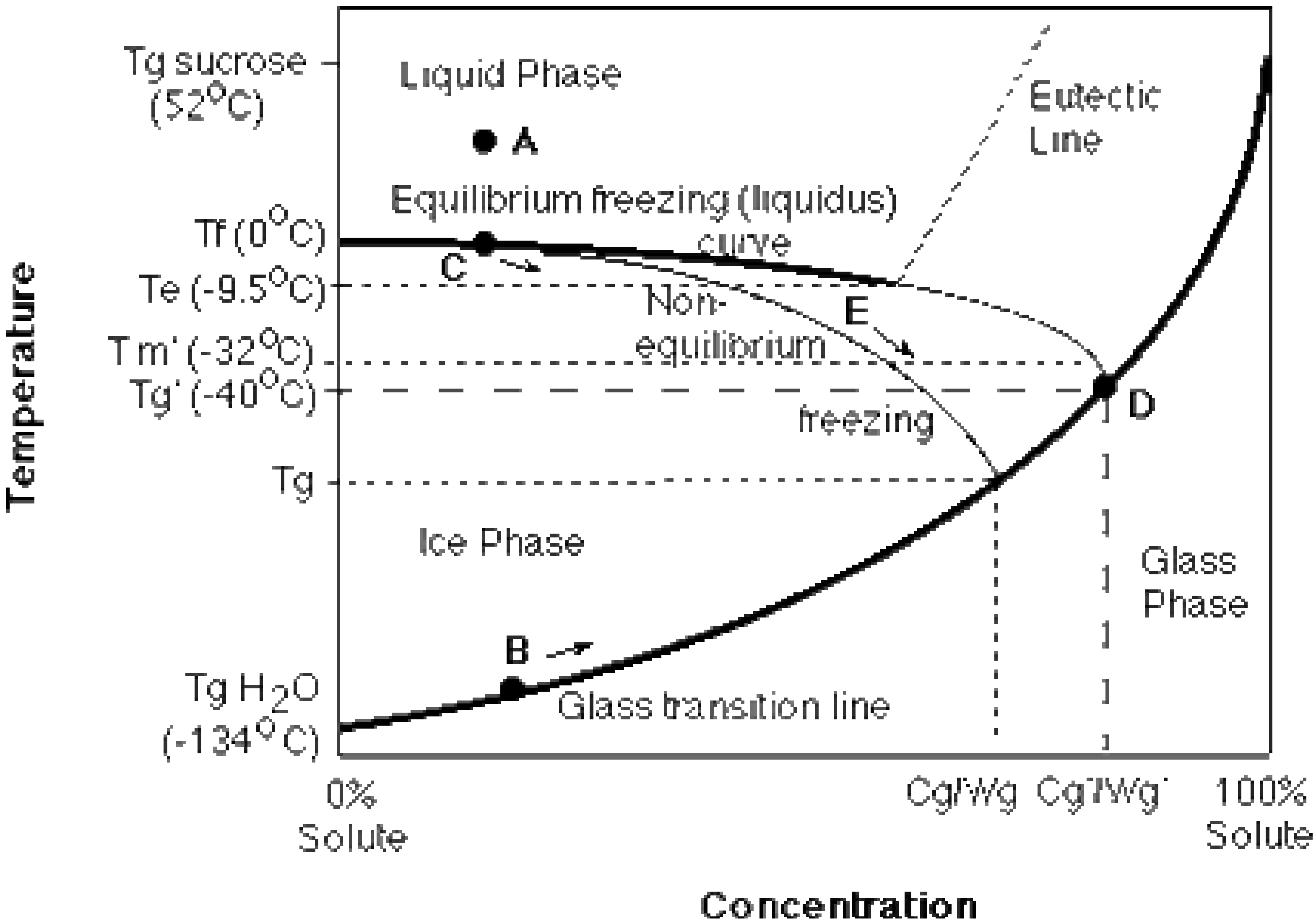
- Temperature where there is no further concentration of solutes due to freezing, thus the solution freezes
- Temperature at which a crystals of individual solute exists in equilibrium with the unfrozen liquor and ice
- Difficult to determine individual eutectic points in the complex mixtures of solutes in foods so term FINAL EUTECTIC POINT is used
- Lowest EUTECTIC temperature of the solutes in the food

Eutectic temperatures

- Ice Cream - 55C
- Meat -50 to -60C
- Bread -70C

MAXIMUM ICE CRYSTALS FORMATION IS NOT POSSIBLE UNTIL THIS TEMPERATURE IS REACHED

Phase transition diagram and Tg



Freezing curve

- Point FG
  - Temperature of the ice water mixture falls to the temperature of the freezer
  - Percentage of water remains unfrozen
- Food frozen below point E forms a glass which encompasses the ice crystals.

Glass transition temperature, Tg

- Glass transition temperature:
  - is the temperature at which the products undergoes a transition from the rubbery to the glassy state
  - Formation of glass protects the texture of the foods and gives good storage stability

Ice Crystals

- The location of ice crystals in tissue is the function of

1. Freezing rate
   - Slow
   - Rapid
2. Specimen temperature
3. Nature of the cell

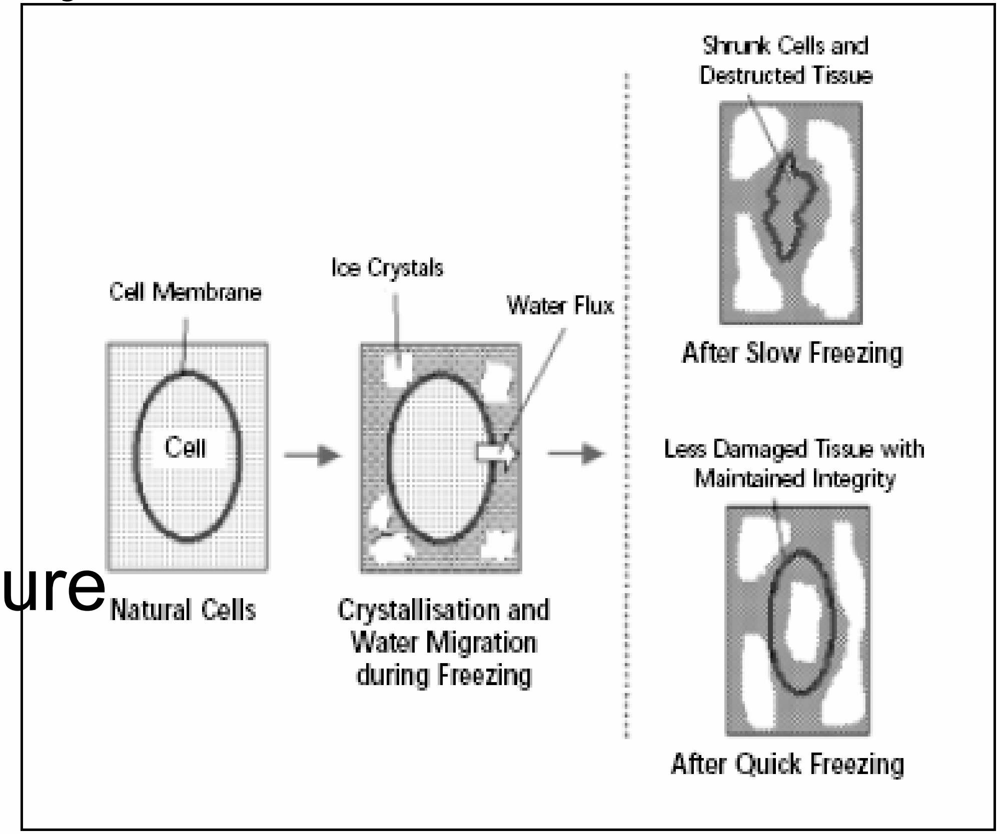


Figure 3. Crucial impact of freezing rate on the end product quality.

K. Fikiin, 2003, Sofia, Bulgaria

Slow freezing

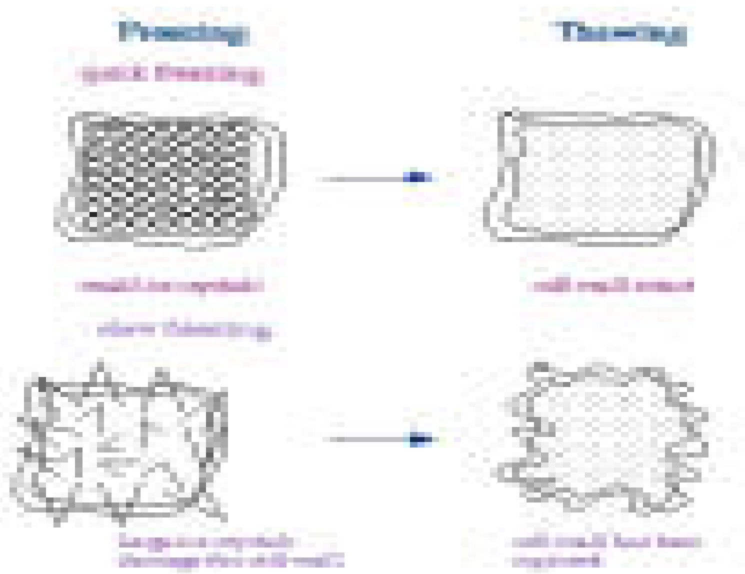
- Rates of cooling of less than 1°C/min
- Ice crystals form in extracellular locations
- Large ice crystals formation
- Maximum dislocation of water
- Shrinkage (shrunk appearance of cells in frozen state)
- Less than maximum attainable food quality

Rapid freezing

- Produces both extracellular and intracellular (mostly) locations of ice crystals
- Small ice crystals
- Numerous ice crystals
- Minimum dislocation of ice crystals
- Frozen appearance similar to the unfrozen state
- Food quality usually superior to that attained by slow freezing

Rapid vs. slow freezing

Rapid freezing



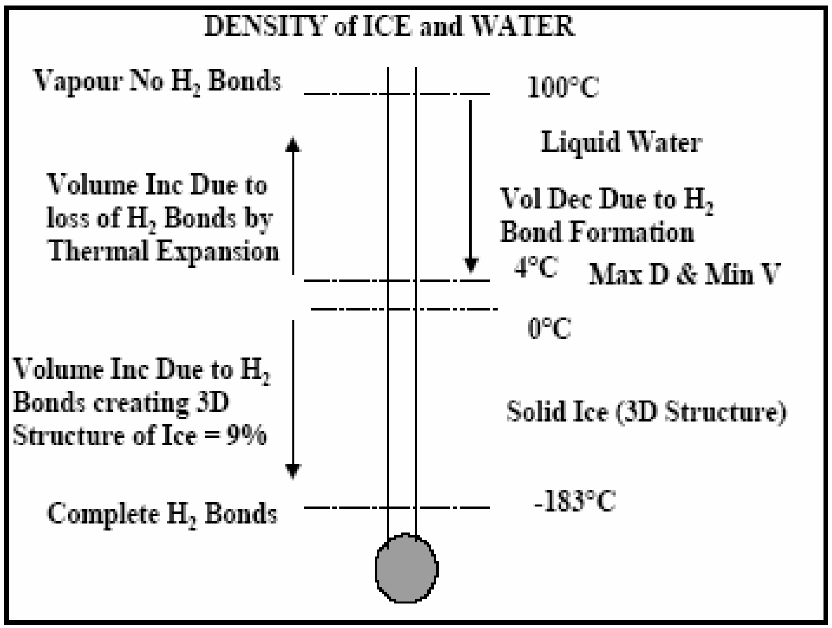
Thawed food

Slow freezing

Volume changes

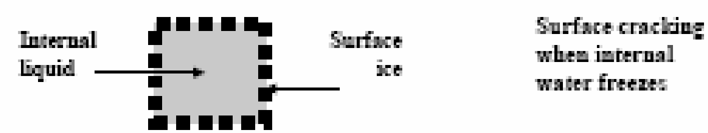
- The volume of ice is 9% greater than the volume of water
- Expansion of foods after freezing would be expected and depends on:
  - Moisture content
  - Cell arrangement
  - Concentration of solutes (higher concentration less expansion)
  - Freezer temperature

Physical effects of freezing



PHYSICAL EFFECTS OF FREEZING
(continued)

3. Recrystallisation (crystals grow during freezing)
   - slow freezing
   - greater during storage
4. Temp gradients



5. Fast freezing rate can damage small pieces

CHEMICAL EFFECTS OF FREEZING

- Concentration of chemicals in liquid phase
- Increased acidity
- Low pH→protein denaturation
- Effect more pronounced during storage and slow freezing

Types of chemical changes

- Flavor and odor deterioration
- Pigment degradation
- Enzymatic browning
- Autoxidation of ascorbic acid
- Protein insolubilization
- Lipid oxidation

Factors that affect chemical changes

- Initial substrate concentration
- pH, Aw, O
- Handling and processing
- Time and temperature

Prevention of chemical changes

- Inactivation of enzymes
- Low temperature storage
- Alternation of pH
- Exclusion of oxygen

MICROBIOLOGY OF FROZEN FOOD

- Growth of microorganisms is temperature dependent.
- No pathogens can grow around ≈5ºC.
- No microorganisms growth <-5º.

MICROBIOLOGY OF FROZEN FOOD

Freezing cannot kill pathogens if food is already contaminated !!!!!!!!!!!!

However:

Some microorganisms are killed

Some are injured

Some are OK

MICROBIOLOGY OF FROZEN FOOD

- During freezing and storage no problem

- After thawing

    controlled (no problem)

    uncontrolled (food safety issues)

MICROBIOLOGY OF FROZEN FOOD

NUMBER OF BUGS SURVIVING FREEZING DEPENDS ON

1. Number of bugs
2. Type of bug
3. Storage temperature
4. Method of measurement
5. Temperature fluctuations→decrease

MICROBIOLOGY OF FROZEN FOOD

SUMMARY

Need to:

- control initial load
- freeze rapidly
- store at -18°C (constant)
- thaw rapidly (low temperature)
- use immediately, or

  *store≈5°C

  *cook

Freezing Foods

- Pre-freezing
- Freezing
- Storage
- Thawing

- Fruits and Vegetables
- Frozen fruits
- Poultry and meats
- Seafood
- Dairy
- Bakery
- Prepared foods

Pre-freezing foods- F&V

- Need to control enzymatic reaction
- Chemical or heat
- Fruits
  - Ascorbic acid
  - Sulfur dioxide
  - Citric acid
- Osmoconcentration of fruits
  - Add sucrose or sugar-syrup
- Vegetables
  - Blanching

Pre-freezing of Muscle Foods

- Seafood
- Prepared to freeze
- Injected w/ cryoprotectant
- Otherwise added cryoprotectant + marinade (tumble) or cryoprotectant + breading

- Poultry
- Prepared
- Injected or tumbled
- Frozen

Factors that affect freezing (rate)

- Characteristics of the food: composition
- Thermal conductivity
- Temperature difference
- Food size (volume to area)
- Insulating effects (air, package

Factors Affecting Freezing Rate

2 Absolute refrigeration required, ie. ability of system to remove heat

3 Temperature difference between product and medium

4 Air velocity

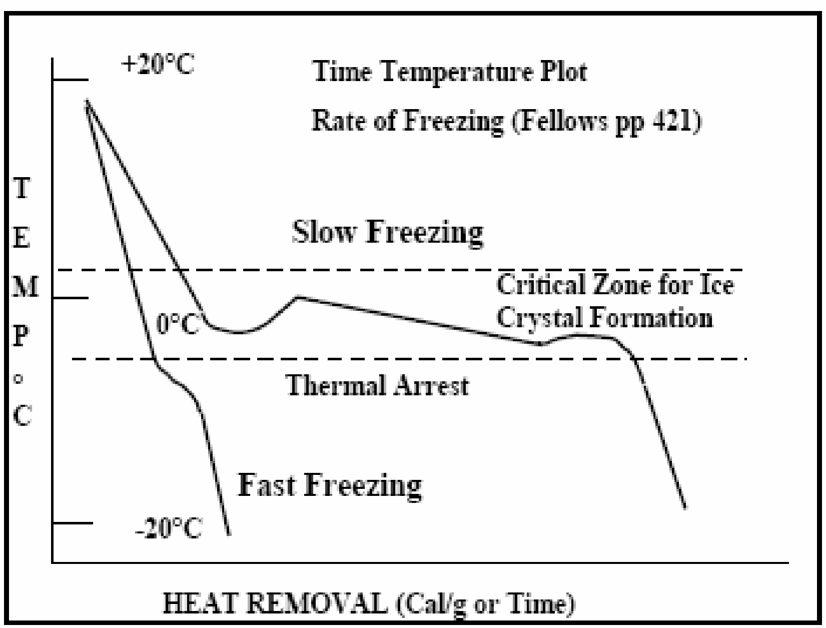
5 Product thickness

6 Contact between product and medium

7 Initial product temperature

Freezing Types (equipment)

- Mechanical
  - Direct
  - Indirect (ammonia, others)
- Cryogenic
  - CO_2
  - N_2



- *Slow freezers* and *sharp freezers* (0.2 cm/h) including still-air freezers and cold stores,
- *Quick freezers* (0.5-3 cm/h) including air-blast and plate freezers,
- *Rapid freezers* (5-10 cm/h) including fluidized-bed freezing and
- *Ultrarapid freezers* (10-100 cm/h), that is cryogenic freezers.

Selection of Freezer Equipment

- $
- Rate of freezing required
- Size, shape, and package
- Batch vs. continuous

Chest and sharp freezers

- Inexpensive
- Temps - 20C and - 30C,
- Slow- no mechanical movement

Blast freezers

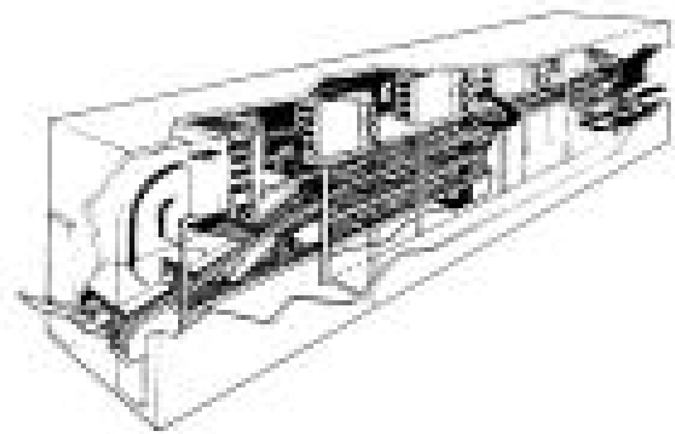
- Temps -30C and -40C at a velocity of 1.5 - 6.00 ms-1
- Many configurations are possible.
- Fast freezing -
- Continuous vs. batch -
- Potential concerns - freezer burn and dehydration (counter current flow helps)

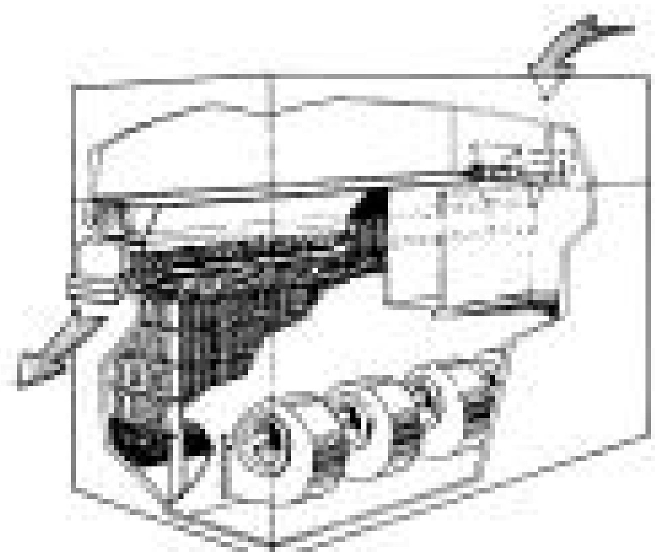
Ice-cream or Scraped -surface freezer

- Prefreezing of fluid products: ice- cream mix
- Finished freezing in the “hardening room”

Belt or Spiral freezers

- There are modified air-blast freezers in which a continuous flexible mesh belt is formed into spiral tiers.
- Spiral freezers require relatively small floor-space and have high capacity (for example a 50-75 cm belt in a 32-tier spiral processes up to 3000kgh-1).
- Other advantages include automatic loading and unloading, low maintenance costs and flexibility for different products. They are used for a wide range of foods including pizzas, cakes, pies, ice cream, whole fish and chicken portions.





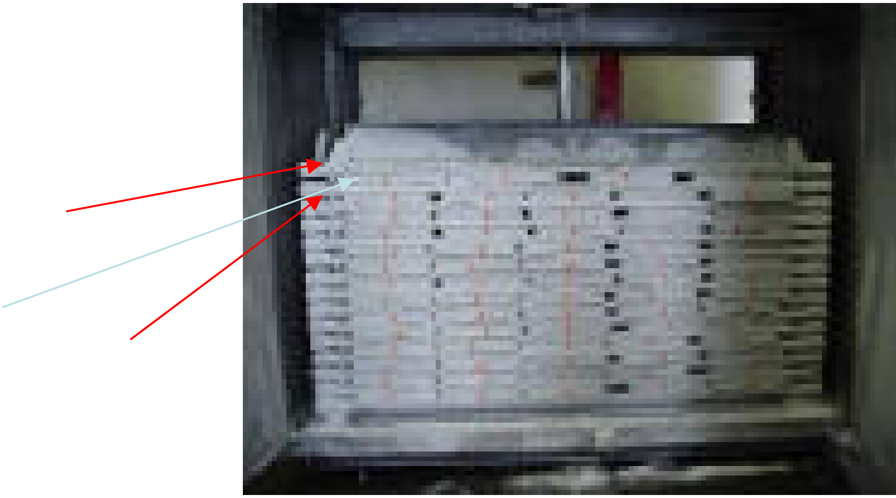
Fluidized Bed freezer

- High air flow velocities: 2-5 m/s Bed depth: 2-13 cm - both are determined by food size and shape.
- Higher heat transfer coefficients, shorter freezing times, higher production rates (I0,000kgh-1) and less dehydration of unpackaged food than blast freezing.
- Limited to particulate foods - obvious

BOC Gases

Plate freezer

- Advantages:
  - good use of floor space
  - low operating costs
  - little dehydration of food
  - high rates of heat transfer
  - food package keeps dimensions
- Disadvantages:.
  - high capital costs
  - size limitations



Cryogenic freezers

- Description: Cryogen may be sprayed on food or food may be immersed in cryogen.
- Most common refrigerants - not fluorocarbons
- Heat content -
- *Liquid nitrogen*: 48% of the total freezing capacity (enthalpy) is taken up by the latent heat of vaporization needed to form the gas; 52% of the enthalpy is available in the cold gas
- *Carbon dioxide:* freezing capacity (85%) is available from the subliming solid

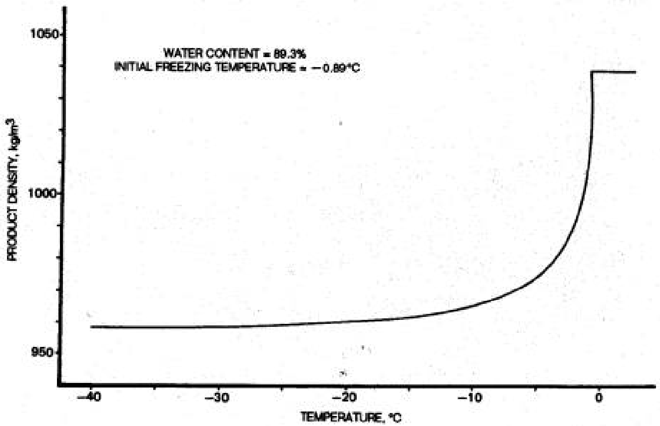
Properties of food cryogens

	Liquid N_2	CO_2
Density (kg m^{-3})	784	464
Specific heat (liquid) (kJ $kg^{-1}K^{-1}$)	1.0	2.2
Latent heat (kJ kg^{-1})	358	352
Total usable refrig. effect (kJ kg^{-1})	690	565
Boiling point (C)	-196	-78.5 (sub)
Consumption per 100 kg of product frozen (kg)	100-300	120-375

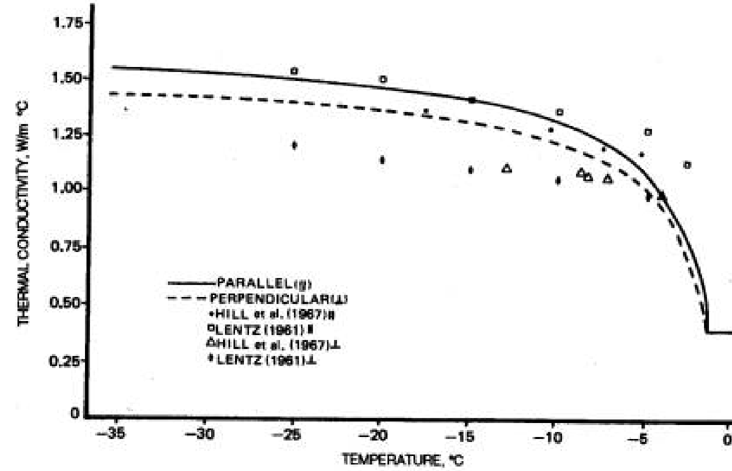
Table 21.3--A comparison of freezing methods

Method of freezing	Typical film heat transfer coefficient	Typical freezing times for specified foods to -18C (min)	Food
Still air	6-9	180-4320	Meat carcass
Blast (5 ms^{-1})	25-30	15-20	Unpackaged peas
Blast (3 ms^{-1})	18		--
Spiral belt	25	12-19	Hamburgers; fish fingers
Fluidized bed	90-140	3-4	Unpacked 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 ca.1mm thick)
Cryogenic (liquid N)		1.5	454 g of bread
	1500	0.9	454 g of cake
		2-5	Hamburgers; seafood
		.5-0.6	Fruits and vegetables

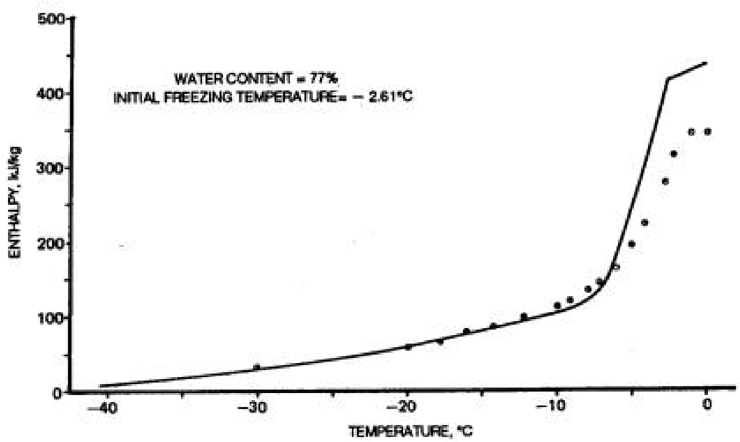
Properties of frozen foods



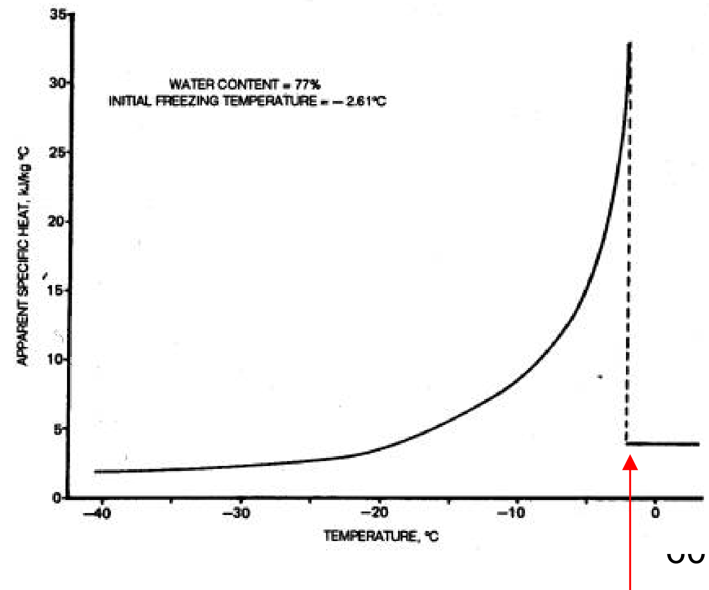
Density



Thermal conductivity, k



Enthalpy, H



(Singh and Heldman, 1993) Specific Heat, Cp

Frozen Food Quality Issues

- **Key factors:**

 - storage temperature – generally the colder the better. (costly)

- temperature fluctuations – avoid!

- **Practical Storage Life (PSL)**

 Defn: Time that the product maintains product sensory quality or functionality. A somewhat vague term.

- **High Quality Life (HQL)**

 Defn: Time from freezing until a statistically significant change in quality is perceived by sensory panel.

- Just Noticeable Difference – (JND) –

The practical storage life of frozen foods as influenced by storage temperature.

(Source: Singh and Heldman, 1993. Introduction to Food Engineering, Academic Press. From IIR International Institute of Refrigeration, 1983, Paris)

Frozen Food Quality

- Pre-freezing
- Freezing
- Packaging
- Storage
- Distribution/Transport
- Retail
- Consumer (Thawing)

The loss in quality of strawberries during a typical manufacturing through distribution chain.

Source: Singh and Heldman, 1993. Introduction to Food Engineering, Academic Press. From: Jul, 1984, The Quality of Frozen Foods

Stage	Time (Days)	Temperature (C)	Acceptability (Days)	Loss per day (%)	Loss (%)
Producer	250	-22	660	0.15152	37.88
Transport	2	-14	220	0.45455	0.91
Wholesale	50	-23	710	0.14085	7.04
Transport	1	-12	140	0.71429	0.71
Retail	21	-11	110	0.90909	19.09
Transport	0.1	-3	18	5.55556	0.56
Home freezer	20	-13	180	0.55556	11.11
Total storage (days)	344.1			Total quality loss	(percent) = 77.30

Defects in frozen foods

- Freezer burn – fluctuations in temperature
- Recrystallization
- Drip loss
- Loss of functionality
- Chemical reactions

Dehydration (freezer burn) is caused by changes in temperature and differences in RH

Shrimp that underwent freezer burn
Frigoscandia Distribution

Recrystallization

- Ice crystals are relatively unstable
- Undergo metamorphic change
- Shape
- Size
- Orientation
- Number
- Causes quality loss in food
- Occurs because systems move towards a state of equilibrium
- Migratory recrystallization
- Major type recrystallization in food
- Caused by a fluctuation in storage temperature

Migratory recrystallization

- Surface of food warms
- Ice on the surface partially melts
- Larger crystals become smaller
- Crystals less than 2mm disappear
- Increases vapor pressure on the surface
- Moisture migrates to lower pressure
- Causes food on the surface to dehydrate
- When temp drops water vapor joins existing ice crystals

Further reading

- Fikiin,K. 2003. http://www.flair-flow.com/industry-docs/sme-syn10.pdf
- The freezing process:
  http://www.ucalgary.ca/~kmuldrew/cryo_course/cryo_chap6_2.html