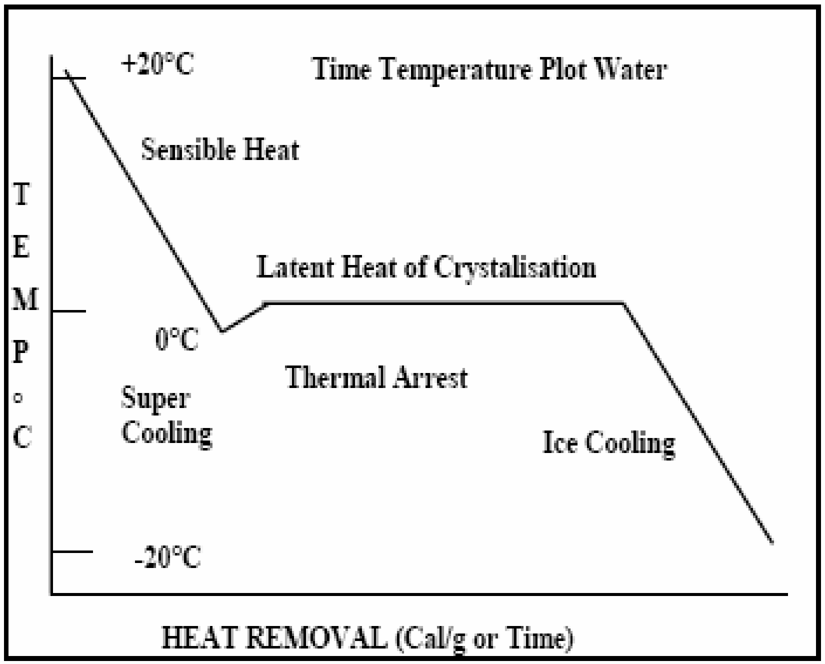
FDE 447
COLD PRESERVATION TECHNOLOGY

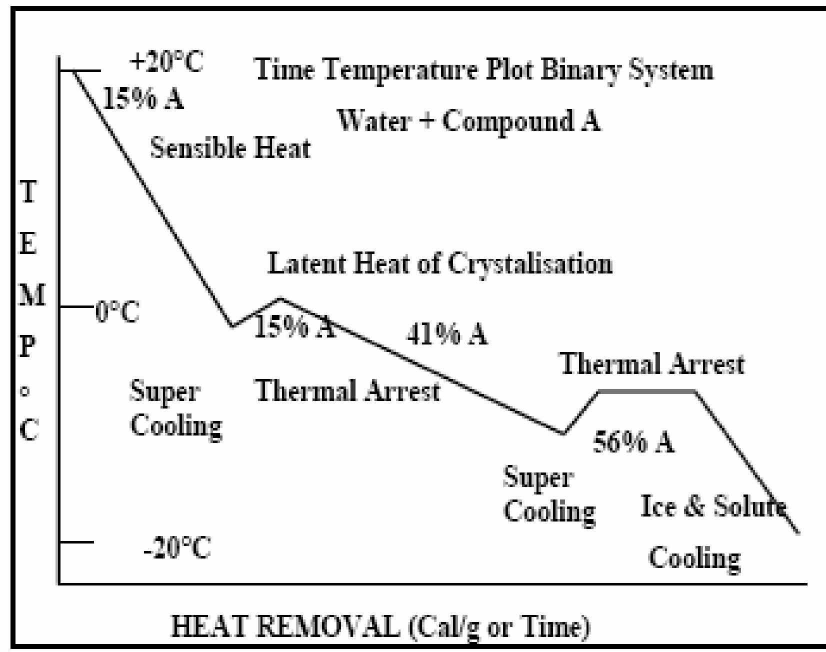
Content:

*Freezing curves
*Slow freezing vs. fast freezing
*Physical effect of freezing

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

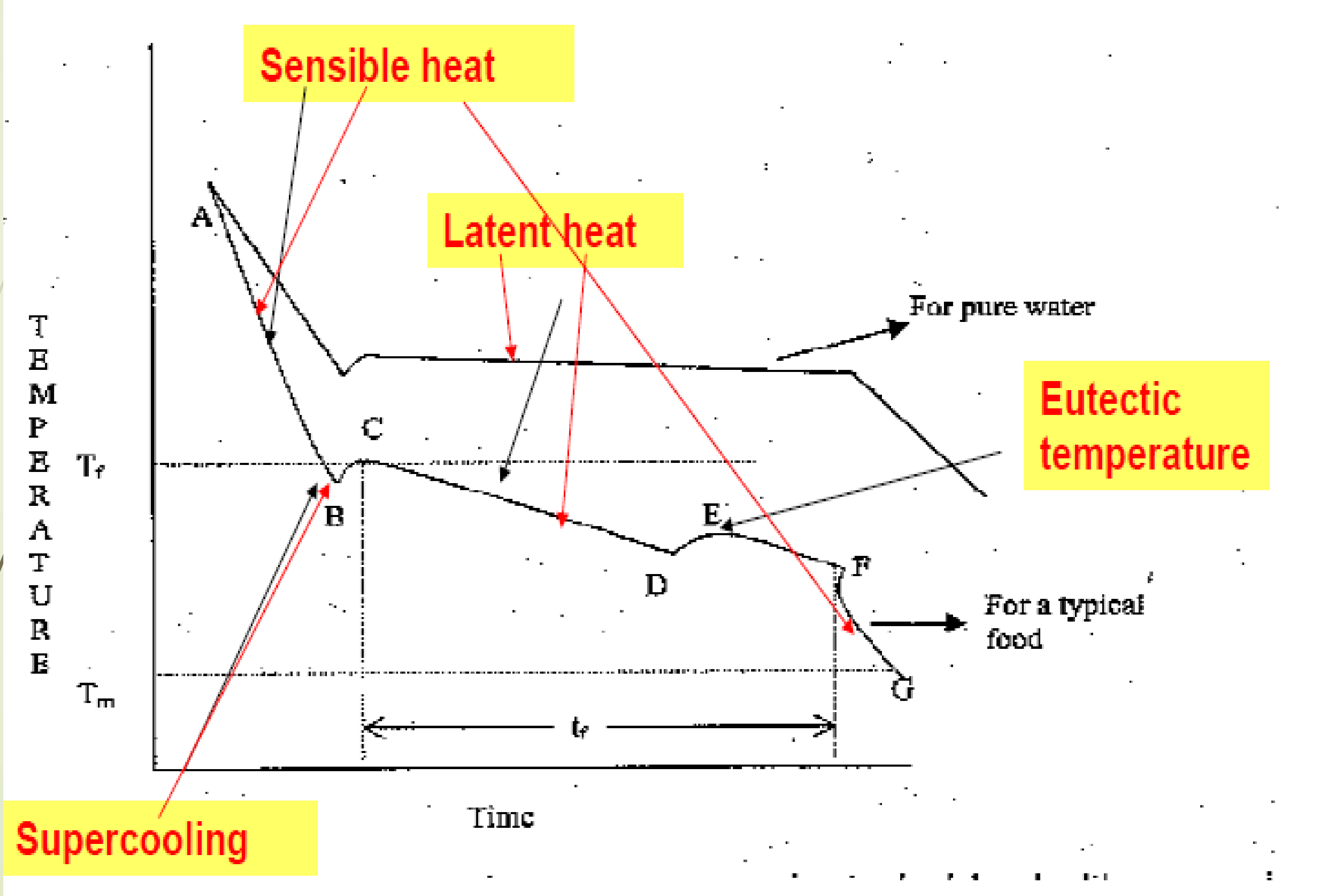


A-water



System B-Binary system

Freezing curve



Freezing curve

Point AB

–Food cooled below freezing point (less than 0°C)

–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)

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

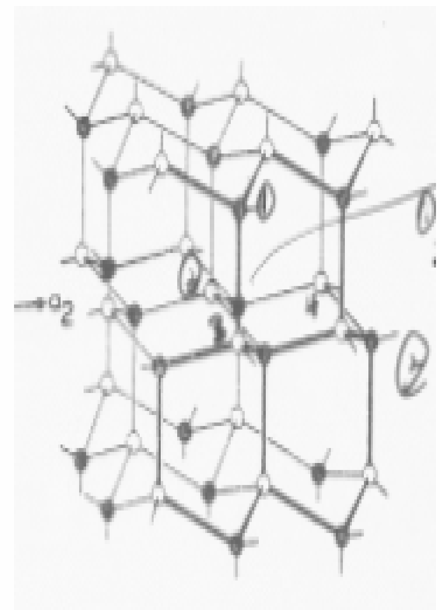
Inter-cellular ice crystals grow

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

<u>Point CD</u>

– 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

<u>Point DE</u>

–One of the solutes becomes supersaturated and crystallizes out.

– Latent heat of crystallization is released 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
  - Ice Cream – 55°C
  - Meat -50 to -60°C
  - Bread -70°C

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

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

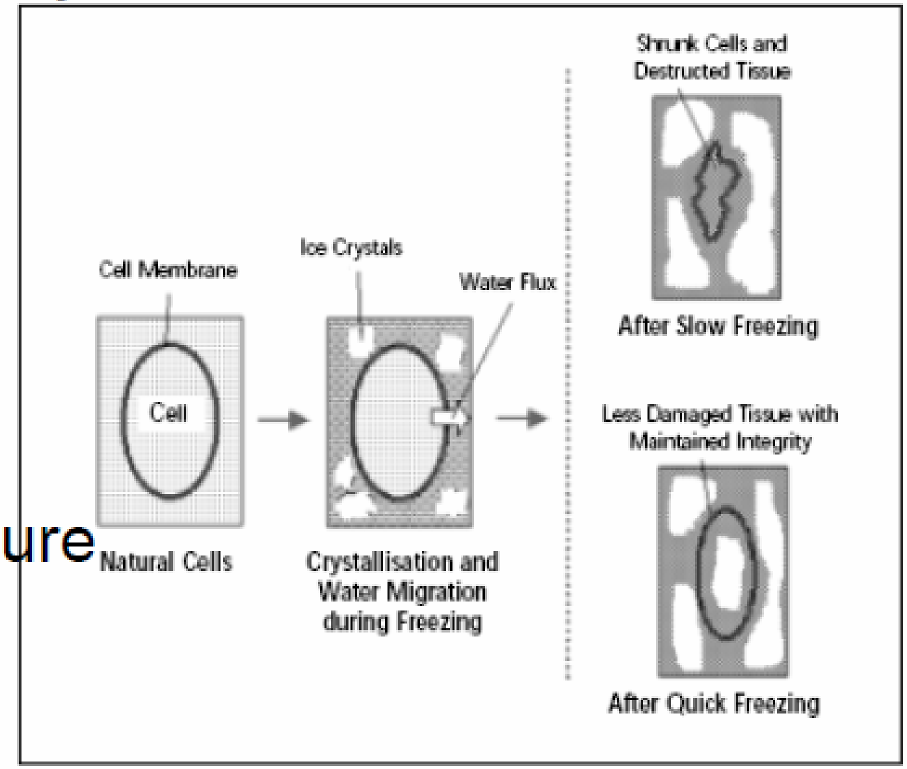


Figure 3. Crucial impact of freezing rate on the end product quality.

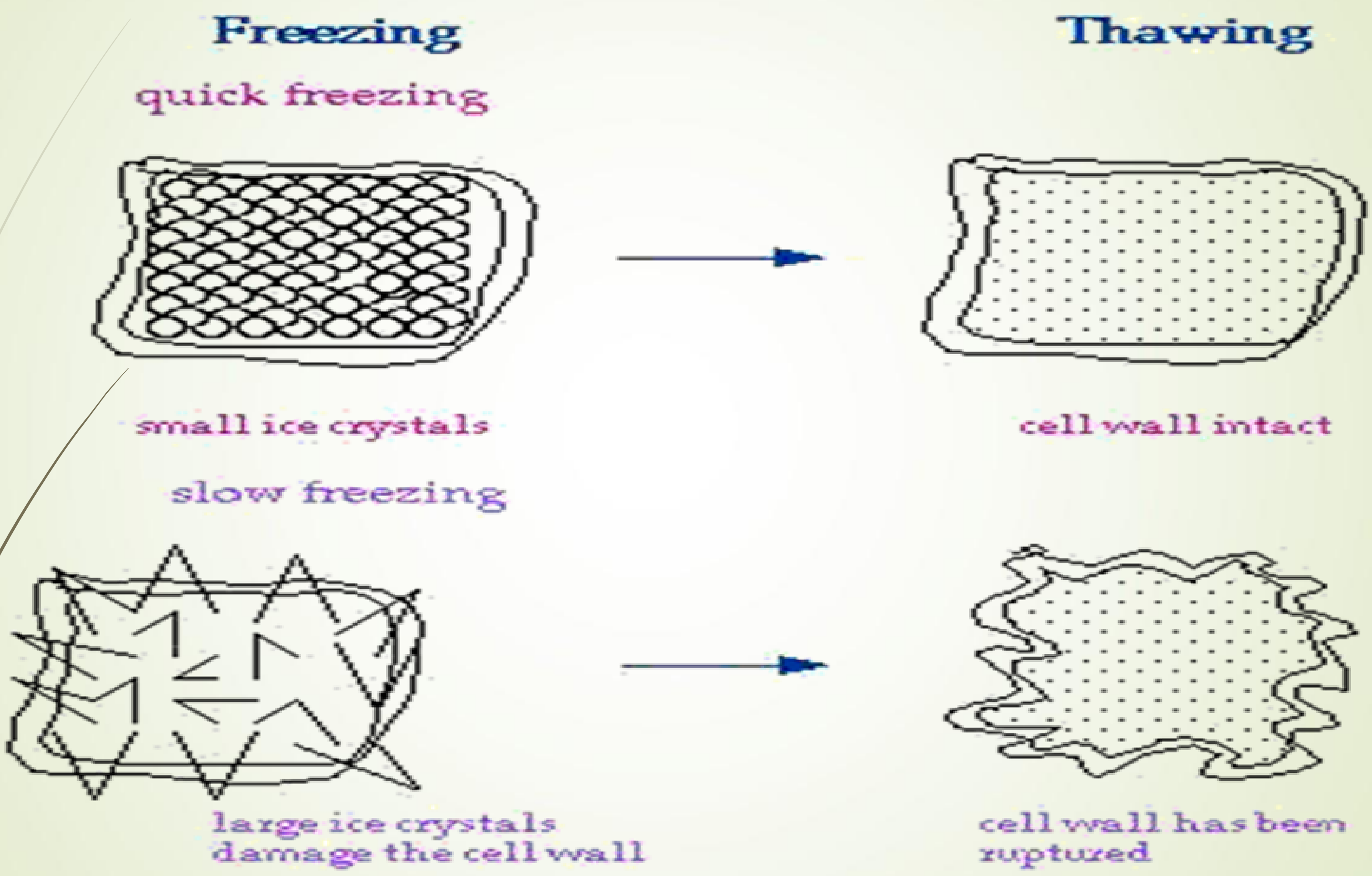
Slow freezing

- 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



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:

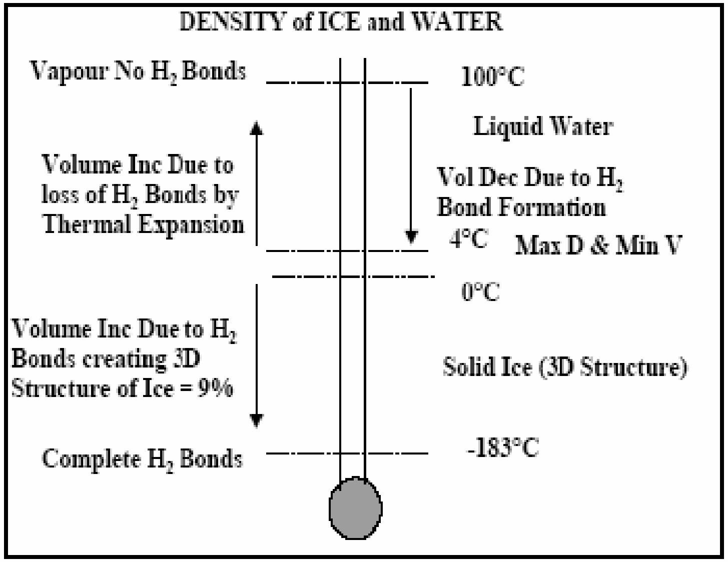
–Moisture content

–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, a_w, O_2
- Handling and processing
- Time and temperature

Prevention of chemical changes

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

Solut 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.

Freezing of foods

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 K) and a high latent heat of crystallisation (334 kJ/ kg). A substantial amount of energy is therefore needed to remove sensible and latent heat to form ice crystals.
- Energy for freezing is supplied as electrical energy, which is used to compress refrigerants in mechanical freezing equipment or to
- compress cryogens.

Freezing of plant tissues

- There are spaces between cells in plant tissues.
- Each cell is surrounded by a semipermeable membrane that holds the solute inside.
- A significant part of the total water in a cell is found in the cytoplasm and vacuole, with small amounts in the membrane, cell wall and spaces between cells.
- When a plant tissue is frozen, there is a chance for ice crystals to form all over the cell.
- However, some factors affect the formation priority of the crystals, depending on the freezing rate.

Freezing of plant tissues

- When freezing a plant tissue, crystallization first occurs in the intercellular space.
- The cell wall and cell membrane act as a barrier against the formation of ice inside the cell.
- Ice formation takes place inside the cell at the latest.
- The high permeability of plant tissue cell walls causes cell desiccation.
- In quick-frozen food, a large number of small ice crystals are formed. Perceived by the eye, it is a lighter color.

Freezing of aminal tissues

- One of the differences between plant cells and animal cells; plant cells contain a "cell wall-cell membrane" complex.
- Animal cells have only the cell membrane and it is flexible.
- Therefore, the formation of intracellular ice crystals is easier in animal tissues.

Freezing of biopolymers

- Hydrocolloids such as starch, protein, pectin, vegetable gums found in foods are defined as biopolymers.
- When biopolymer solutions freeze, the biopolymer concentration rises as a result of the water turning into ice crystals.
- The probability of formation of intermolecular cross-links increases.
- The solubility of the molecules decreases.

Definiton of freezing time of foods

- When the freezing point of a food is mentioned, the freezing starting point, that is, the temperature at which the first ice crystals form is understood.

- Freezing in solutions and foods begins at the freezing point, continues at gradually decreasing temperatures, and finally ends at a very specific temperature called the eutectic point.

- The freezing temperatures of all foods vary between -0.5 and -3°C. But it is difficult to give numbers for processed foods.
- Freezing points of foods can be determined experimentally or with some developed equations.

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

Freezing point of fruits and vegetables, T_f

$$T_f = 287.56 - 49.19\ m_w + 37.07\ (m_w)^2$$

Where: T_f : Freezing point of fruit or vegetable, K

m_s : mass fraction of water in fruits or vegetables

Freezing point of fruit or vegetable juices, T_f

$$T_f = 120.47 + 327.35\ m_w - 176.49\ (m_w)^2$$

Where: T_f : Freezing point of fruit or vegetable juice, K

m_w : mass fraction of water in fruit or vegetable juice

Freezing point of meat, T_f

$$T_f = 271.18 + 1.47\ m_w$$

Where T_f : Freezing point of meat, K

m_s : mass fraction of water in meat