Freezing and Quality of Frozen Foods

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101°, Rure Unsweelener Orange Juice Frozen Concentrated 12 FL 02. (355 mL) In states

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Understanding Freezing

- Retard deterioration of foods preservation
 Chemical, physical, microbial, etc.
- Improve organoleptic properties
 - Desirable characteristics





Controlling Freezing

- Maximal quality of product
 - Initial freezing process
 - Storage and distribution conditions
- Efficient and economic processing



Understanding Freezing of Foods

- Water and phase/state diagrams
- Freezing
 - Mechanisms
 - Rates
- Freezing and food quality
- Storage of frozen foods



Food Freezing

- For a food to freeze, must lower the temperature below its freezing point
- Foods are mixtures of various ingredients, some of which affect phase behavior of water
 - Sugars, salts, proteins, fats, flavors, etc.
- Freezing point depression
 - Dependent on composition
 - Particularly smaller molecular weight ingredients like sugars and salts

Average Freezing Pointsof Some FoodCategories

Food	X (%)	T _f (°C)	
Vegetables	78to 92	-08to-28	
Fruits Apple juice Apple sauce Apple juice co r entrate	87to 95 872 828 498	-09to-27 -1.44 -1.67 -113	
Meat	55to 70	-1.7 to -2.2	
Mil k	87	-0.5	
Egg	74	-0.5	

Freezing

- As freezing proceeds, heat is released and concentration of unfrozen liquid phase increases
 - Phase change (333.2 kJ/kg of ice) causes temperature of local environment to increase
 - Temperature increase depends on amount of ice freezing and the rate of heat removal
 - Freeze concentration of remaining fluid phase causes decrease in freezing point of remaining liquid

Freezing Point Depression



Freezing

- As more heat is removed, the unfrozen phase continues to become more concentrated
- Continued freezing causes decrease in molecular mobility (increase in viscosity of unfrozen phase)
 - Molecules move more slowly
 - Approaches glassy state where molecular mobility is very low

Glass Transition



Freezing

- The endpoint of freezing is either:
 - When freezing point temperature reaches freezer temperature
 - Product temperature goes below the glass transition temperature and the unfrozen phase becomes glassy
- A *state diagram* helps understand which will occur
 - Follow "trajectory" of freezing process





State Diagram

- State diagrams tell us where to expect the system to head for phase equilibrium
 - At a given storage temperature, the system will move to approach the equilibrium curve
 - Maximum amount of ice formed
- Any point other than on the freezing point depression curve, including the glassy state, is nonequilibrium metastable
 - Stability depends on process/storage conditions

Freezing Rate

- But freezing rate determines how much of the allowable water freezes in a food
- Slow freezing equilibrium ice formation
 Follows freezing point depression
- Fast freezing any amount of ice, depending on freezing rate
 - Any trajectory



Water Frozen

- Amount of water frozen into ice thus depends on freezing rate
 - Slow freezing -
 - maximum ice
 - Fast freezing -
 - any ice content



Unfreezable Water assuming phase equilibrium

All products have some water that remains unfrozen even at very low temperatures (<-40°C)

 Meat, fish^a
 8-12%
 Liquid eggs^a
 7%
 fruit juice^a
 3%
 spinach^a
 2%
 white bread^a
 46%
 bread @ -18°C^b

^a Zaritzky, 2000
^b Kennedy, 2000
Both in CJ Kennedy, Managing Frozen Foods (2000)

Freezing Rate

- Due to conduction heat transfer, the freezing rate is also a function of the position in the food
 - Center sees much slower freezing rate than surface
 - Mechanisms of freezing may be different
 - Ice distribution may also be different at surface from interior
 - Temperature differential allows moisture migration



Freezing Rate

- Freezing rate defined as:
 - Ratio between the minimum distance from the surface to the thermal center, and the time elapsed between the surface reaching 0°C and the thermal center 10°C colder than the temperature of initial ice formation. (International Institute of Refrigeration, as quoted by Zaritzky, 2000)
- Typical food freezing rates

– 0.2 - 0.5 cm/h	slow	static
– 0.5 - 3 cm/h	quick	air blast and plate
– 5 - 10 cm/h	rapid	IQF fluidized bed
– 10-100 cm/h	ultra-rapid	cryogenic

Question

- Freezing rate has many impacts on a freezing operation how many can you list?
 - Product quality
 - Throughput rate
 - Refrigeration costs
 - Equipment costs
 - Others?

Freezing Mechanisms

- The process of freezing requires these steps:
 - Subcooling bring temperature down below freezing temperature
 - Nucleation formation of the smallest crystals from the liquid state
 - Growth increase in size of those nuclei until the system approaches phase equilibrium
 - **Ripening** change in dispersion of crystal sizes with time due to thermodynamic effects

Subcooling

- Nuclei do not form under most circumstances until temperature is lowered substantially below the melting point
 - Related to an energy barrier to be overcome to form a stable nucleus
 - The temperature at which nuclei form depends on process conditions
 - Cooling rate, agitation, etc.



Subcooling

- High ΔT (20-30°C)
 - Rapid freezing
 - High nucleation rate
 - Many nuclei formed



CONCENTRATION

- Low $\Delta T (1-5^{\circ}C)$
 - Slower freezing
 - Lower nucleation rate
 - Fewer nuclei formed



Nucleation

• Onset of nuclei formation in a frozen food is when the water molecules attain the correct energy and position to form into a crystal lattice



Higher density

Lower density



Homogeneous nucleation - water molecules cluster together Heterogeneous nucleation - dust particles promote nucleation



Growth

- After nuclei form, they grow until all subcooling has been relieved
 - Equilibrium temperature and product temperature are the same
- Mechanisms
 - Heat removal rate
 - Counterdiffusion of solutes



Effects of Freezing on Food Quality

- Numerous changes take place during all stages of freezing that can affect food quality
 - Prefreezing conditions
 - Freezing rate
 - Storage conditions

Prefreezing

- If initial temperature is well above the freezing point when a product is frozen
 - Water migration occurs due to thermal gradients during cooling and freezing
 - The warm water inside migrates toward surface
 - Redistribution of solutes
 - May be a problem in regions of different water content, e.g., crumb and crust
 - Can cause separation and unsightly appearance

Freezer Bloom

- Freezing of frozen cakes with sugar frosting
 - Freezing from warm state causes water migration, which carries dissolved sugar
 - When the water evaporates (or ice sublimes) leaves unsightly spots



Freezing

- Freezing affects properties of the food
 - Effects on cell structure
 - Osmotic pressure differences between intracellular and extracellular fluid cause moisture migration

– May lead to cell lysis (rupture)

- Moisture migration
 - Osmotic differences; thermal gradients; etc.
- Volume expansion of ice may rupture cells
- Freeze concentration of solutes in unfrozen phase
 - Salts, sugars, etc. may lead to crystallization
- Protein denaturation
 - Freeze concentration of solutes like salts

Slow vs. Rapid Freezing

- Rapid freezing leads to formation of many more and smaller crystals
 - Fewer internal changes in structures (cells, etc.)
 - Smoother product



Freezer Storage

- Over time, changes can occur in the frozen product that cause product quality to deteriorate
 - Equilibration of ice phase volume
 - Changes in ice crystal dispersion due to ripening
 - Starch retrogradation
 - Protein denaturation
 - Water migration and loss

Phase Equilibration

- If phase equilibrium was not attained during freezing, the system will drive towards that equilibrium over time if $T > T_g'$
 - Increase in ice content
 - Changes in ice crystal size distribution

Temperature



Recrystallization

Definition:

"Any change in the number, size, shape, orientation or perfection of crystals following completion of initial solidification." (Fennema, Powrie and Marth, 1973)

 Enhanced dramatically by fluctuating temperatures during storage



Fluctuation in Ice Content



Recrystallization

- Effects of recrystallization
 - Increase in mean size causes disruption of microstructure and loss of texture
 - Smooth frozen product becomes coarse





Moisture Migration and Freezer Burn

- During freezing and frozen storage, regions of different water activity tend to equilibrate
 - Crust and crumb will change during storage
 - Bread and icing or filling
 - Pizza crust and sauce
- Freezer burn color and quality change
 - Loss of moisture to air



Summary

• An understanding of the physico-chemical factors that affect quality during freezing allows production of the highest quality product with the most efficient process