Freezing

Outline

• Examples of freezing in daily life
• Purpose of freezing
• Stages of freezing
• Effect of freezing on properties
• Types of freezers
• Freezing medium
• Shelf life and quality of frozen foods
• Equipment to characterize freezing
• Effect of solids on freezing point of solution
• Determination of freezing time

Examples in Daily Life

• Ice rink
  – 9,000 gallons of -9 ºC brine
  – 5 miles of pipes
  – 270 tons of cooling (1 ton of refrigerant = 3516.8 W)
  – Humidity and temperature control needed
  – Ice hockey versus ice skating (load, impact)
• Earth’s surface
  – 10.4 % is covered with ice
  – 20% is permanently frozen
  – Thickness of ice covering Antarctica (avg. temp. ~ -37 ºC)
    • Average: 2164 m; Max: 4785 m (>10 times height of Sears tower)
    • ~63 m rise in ocean level if all ice melted; add ~7 m for Greenland; not much in arctic
• Does the water inside animals living in extreme cold, freeze?
• Do hot water pipes burst before cold water pipes in winter?
• Can the engine coolant or fuel in our car freeze?
• Does Niagara Falls freeze?
• How does an ice maker work?
• How does a frost-free freezer work?
• How does a snow-maker at a ski slope work?
• How does a de-icer (for cars and planes) work?
Examples in Daily Life (contd.)

- Ice as an insulator
  - Igloo
  - Freezing of pond (do fishes survive? What does wind do?)
- Depression in freezing point
  - Salting of roads during winter
- Freezing foods
  - Blue ice, gel pack, dry ice, liquid nitrogen
  - How is a popsicle made?
- Safety of using liquid nitrogen (in a room or car)
  - 10 liter dewar spilt in a 17 x 17 x 8 room
    - Reduces oxygen level to < 19.5% (need to use respirator)
- Freeze drying of milk/coffee powder
  - Lower the temperature and use vacuum to sublime ice

Freezing

- Purpose of freezing of foods
  - To slow down rates of detrimental reactions by lowering temperature and water activity ($a_w$)
    - Microbial spoilage
    - Enzyme activity
    - Nutrient loss
    - Sensorial changes
  - Prolongs shelf life beyond that of refrigerated foods

*Water activity ($a_w$): Amount of water available for reactions; $a_w$ = equilibrium relative humidity

*Guideline: Generally, rates of reactions double for every 10 °C rise in temperature

Effect of Temperature on Shelf Life

![Graph showing the relationship between temperature and shelf life](image)
**Freezing of Foods**

- Quality of frozen food depends on
  - Rate of freezing (°C/hr)
  - Ambient storage (freezing medium) temperature ($T_s$)
  - Constancy of temperature (cycling of temp. is not good)
- Factors affecting rate of freezing (°C/hr)
  - Convective heat transfer coefficient ($h$)
  - Ambient storage (freezing medium) temperature ($T_s$)
- Advantages of rapid freezing
  - Smaller ice crystals are formed
    - Thus, less structural damage to product
  - Prevents concentration (of sugars, fats etc.)
- Freezing time
  - Time taken to freeze majority (~95%) of product
    - A product is never completely frozen (~5-10% unfrozen)

**Shelf Life**

- High Quality Life (HQL)
  - Period of frozen storage when a difference in quality can just be detected
- Practical storage life (PSL)
  - Period of frozen storage during which product retains its characteristics and is suitable for consumption
  - At -12 °C
    - PSL = ~4 months for fruits and seafoods
    - PSL = ~6 months for vegetables
    - PSL = ~8 months for meats
- Typical frozen storage temperature
  - Fruits and vegetables: ~ -18 °C
  - Ice cream and fatty fish: ~ -25 °C

**Freezer Burn**

- Refers to moisture loss as ice crystals sublimate from surface
  - Produces brownish spot as tissue becomes dry
  - Could cause off-flavors
  - It is a quality issue and not a safety issue
  - Moisture resistant wrap can prevent freezer burn
Stages of Freezing

- Super-cooling or under-cooling
  - Cooling slightly below initial freezing point
- Nucleation
  - Formation of ice crystals
- Crystal growth
  - Increase in size of ice crystals
- Maturation
  - Stabilization of ice crystals

Ice-crystal seeding is sometimes done to initiate and accelerate freezing

Freezing Curve

% Water Frozen at Different Temperatures
Properties of Frozen Foods

- As temperature decreases
  - Density decreases
  - Enthalpy decreases
  - Apparent specific heat decreases
  - Thermal conductivity increases
Apparent Specific Heat of Sweet Cherries as a function of Temperature

![Graph showing apparent specific heat of sweet cherries as a function of temperature. Initial freezing temperature is -2.6°C.](image)

Thermal Conductivity of Lean Beef as a function of Temperature

![Graph showing thermal conductivity of lean beef as a function of temperature.](image)

Types of Freezers

- Direct contact (Usually Individual Quick Freeze -- IQF type)
  - Air blast
  - Fluidized bed (particles on mesh conveyor; air from below)
  - Immersion (N₂, CO₂, Freon)
    - Fastest, but most expensive
- Indirect contact
  - Plate (usually, food is within package)
    - Apply pressure on plates to minimize resistance to heat transfer
  - Air blast (usually, food is within package)
  - Scraped surface heat exchanger
    - Jacket (evaporator) has refrigerant
    - 60-80% of latent heat is removed
    - Product exits as a slurry

Freezers can be batch or continuous
### Freezing Medium

- **Ice**
  - At atmospheric pressure, melting point is 0 °C
  - Latent heat of fusion = 6,003 J/mol = 333.5 kJ/kg
- **Liquid nitrogen**
  - At atmospheric pressure, boiling point is -195.8 °C
  - Latent heat of vaporization = 5,580 J/mol = 199 kJ/kg
- **Dry ice (solid CO₂)**
  - At atmospheric pressure, sublimation point is -78.5 °C
  - Latent heat of sublimation = 25,214 J/mol = 571 kJ/kg

### Equipment to Characterize Freezing

- **Refractometer**
  - Used to determine total solids (or sugar) in solution
- **Cryoscope**
  - Used to determine initial freezing point of solution
- **Differential Scanning Calorimeter (DSC)**
  - Used to determine freezing point, specific heat, latent heat, apparent specific heat

### Adding a Solute to a Solvent

- When a solute is added to a solvent
  - The vapor pressure of the solvent decreases
    - Raoult’s law: Partial pr. of solvent ∝ mole fraction of solvent
- **Colligative properties**
  - Properties of solutions that depend on relative number of solute particles to solvent particles
    - Lowering of vapor pressure
    - Elevation in boiling point
    - Depression in freezing point
    - Osmotic pressure
Depression in Freezing Point ($\Delta T_f$)

- Addition of a solute (say, salt) in a solvent (say, water) decreases freezing point by a magnitude $\Delta T_f = T - T'$ given by the Clausius-Clapeyron equation:

$$\ln(X_w) = \frac{\lambda_{\text{fusion (water)}}}{R_g} \left[ \frac{1}{T} - \frac{1}{T'} \right]$$

$X_w$: Mole fraction of water

$\lambda_{\text{fusion (water)}}$: Latent heat of fusion of solvent (water)

$\lambda_{\text{fusion (water)}}$ at atmospheric pressure = 6,003 J/mol = 333.5 kJ/kg

$R_g$: Universal gas constant = 8.314 J/mol K

$T$: Freezing point of pure solvent (water) in Kelvin; $T = 273$ K

$T'$: Freezing point of solution after adding solids (in Kelvin)

X-w: Mole fraction of water

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Mole Fraction of Water ($X_w$)

$$X_w = \frac{m_w / M_w}{m_w / M_w + m_s / M_s}$$

- $m_w$: Mass of water
- $M_w$: Molecular weight of water (=18 g)
- $m_s$: Mass of solute
- $M_s$: Molecular weight of solute

Note: $m_w / M_w$ is the no. of moles of water and $m_s / M_s$ is the no. of moles of solute

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Depression in Freezing Point ($\Delta T_f$) for Dilute Solutions

$$\Delta T_f = T - T' = k_f (m)$$

$k_f$: Molal freezing point constant of solvent (water)

($k_f = 1.86 \degree C/mol$ for water)

$m$: Molality (no. of moles of solute per kg solvent)
**Ways of Expressing Concentration of a Solution**

- Molality
  - No. of moles of solute per kg solvent
- Molarity
  - No. of moles of solute per liter of solution
- Normality (for reactions)
  - No. of gram equivalent weights of solute per liter of solution
  - Normality = (Molarity) x (No. of protons exchanged)
- Formality
  - No. of formula equivalent weights of solute per liter of solution
  - Formality = Molarity except for ions

**Freezing Time (t_f): Plank’s Equation**

\[ t_f = \frac{\rho_f \lambda_{fusion} (product) \left[ \frac{P'}{a} + \frac{R'}{a^2} \right]}{h} \]

- \( \rho_f \): Density of frozen product, kg/m³
- \( k_f \): Thermal conductivity of frozen product, W/m K
- \( \lambda_{fusion} (product) \): Latent heat of fusion of product, J/kg
- \( \lambda_{fusion} (product) \sim (\% \ moisture) \times (\lambda_{fusion} (water)) \)
- \( T_f \): Initial freezing point of product, K
- \( T_a \): Temperature of freezing medium, K
- \( h \): Convective heat transfer coefficient, W/m² K

- Sphere: \( a = \text{diameter}, \ P' = 1/6, \ R' = 1/24 \)
- Infinite cylinder: \( a = \text{diameter}, \ P' = 1/4, \ R' = 1/16 \)
- Infinite slab: \( a = \text{thickness}, \ P' = 1/2, \ R' = 1/8 \)

**Plank’s Equation (Assumptions)**

- At \( t = 0 \), the product is at its initial freezing point
  - Time for removal of latent heat is determined
    - Time for removal of sensible heat is not accounted for
      - This can be calculated using Heisler chart
- Freezing takes place in 1 dimension (direction) only
  - Thus, 1-D shapes: Sphere, infinite cylinder, infinite slab
- Density and thermal conductivity of the product remain constant during freezing
Summary

- Purposes of freezing
  - Slowing down rates of reactions (by lowering temperature and time)
  - Microbial spoilage, enzyme activity, nutrient loss, senescent changes

- Quality of frozen food depends on
  - Rate of freezing (°C/hr), freezing medium temperature ($T_i$), constancy of temperature (cycling of temp. is not good)

- Factors affecting rate of freezing (°C/hr)
  - Convective heat transfer coefficient ($h$), freezing medium temperature ($T_a$)

- Advantages of rapid freezing
  - Smaller ice crystals formed (thus, less structural damage to product), prevents concentration (of sugars, fats etc.)

- Stages of freezing
  - Super-cooling, nucleation, crystal growth, maturation
  - As temperature decreases
    - Density, enthalpy, apparent specific heat decreases; thermal conductivity inc.

- Types of freezers
  - Direct contact: Air blast, fluidized bed, immersion
  - Indirect contact: Plate, air blast, scraped surface

- Adding solute to solvent decreases freezing point (depends on mole fraction of solvent)

- Freezing time calculation using Plank’s equation
  - Time for latent heat removal only, 1-D freezing, constant properties ($k$, $\rho$)
  - Time for sensible heat removal can be determined using Heisler charts