# Freezing and Frozen storage of Fish and Shellfish Products

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Low temperature preservation is the best method to retain the quality and freshness of fish and fish products for a long time. Among them, chill storage i.e., keeping the fish in the unfrozen condition has only limited shelf life and it will vary between 4 and 20 days depending on the condition and species of fish. In frozen storage also the shelf life is restricted but it varies from few weeks to years. The various factors that affect the frozen storage shelf lives are condition of fish at the time of catch, handling, processing and product development, packaging and glazing of the product, freezing method adopted, frozen storage temperature, stacking methods and transportation techniques. These factors can be put together and can be termed as 'Product, Processing and Packaging' (PPP) and 'Time Temperature Tolerance' factors (TTT).

## Freezing Characteristics

The water present in fish products are converted to ice during freezing i.e., a change from the liquid phase to the solid phase. The change of water from liquid to solid phase results in increase in volume and a consequent decrease in density, increase in thermal conductivity and thermal diffusivity, and decrease in heat capacity. The volume increase on freezing of water is by about 9%, thermal conductivity 4 times and thermal diffusivity 11 times. Heat capacity is found to reduce from one cal/g to 0.5 cal/g. A proportional change in these properties may also observed in food products.

Since water is the major component undergoing changes during freezing, knowledge of the effect of pressure and temperature on the phase diagram of water is necessary. Various combinations of temperature and pressure on two or three states of water in equilibrium are given in Fig. 1.

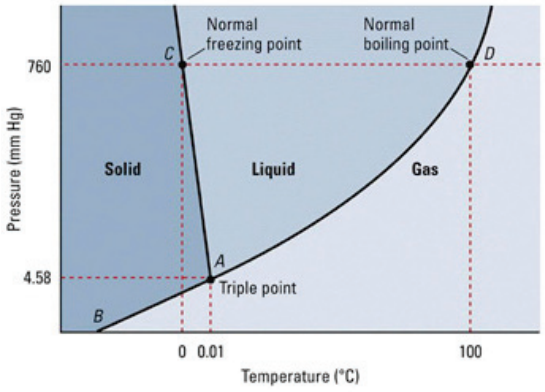


**Fig. 1. Pressure temperature phase diagram of water**

The normal atmospheric pressure lowers the freezing point of water by 0.0075°C. The dissolved air at one atmospheric pressure depresses the freezing point of water by 0.0024°C. Thus at 4.578 mm Hg pressure the freezing point of water is 0.0099°C greater than that at one atmosphere. This point is called triple point where all three phases of water exist in equilibrium.

## Freezing Curve for Pure Water

The freezing curve of pure water is given in Fig. 2. During the early stages of cooling i.e. cooling from ambient temperature to 0°C (T1 to T2) the sensible heat amounting to 1cal/g° C is removed. Point S represents super cooling. Super cooling is needed to remove sufficient quantity of heat so as to get stable ice nuclei for crystal growth. On crystallization of ice at S the heat of crystallization is released and the temperature of the system rises to 0°C (T2) from S. The temperature remains at 0°C until all the water is converted to ice. This period is called thermal arrest period. 79.8 cal of heat must be removed for each gram of ice formed. The water-ice transformation usually involves a long period. On completion of solidification further heat removal is faster and about 0.5cal/g of heat is removed for the decrease by every 1°C.

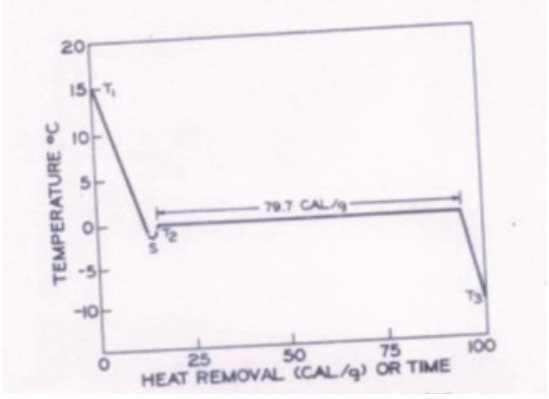


**Fig.2. Freezing curve for pure water**

The freezing point of water in fish is not at 0°C, but is around -1°C depending on the concentration of solutes in fish muscle. Table 1 gives the approximate amount of water frozen at various freezing temperatures. It can be seen that at a temperature of -30°C about 8% of water remains unfrozen.

**Table 1. Percentage of water frozen at various temperatures in a typical fish fillets with 80% water**

| Temperature (°C) | Frozen water (%) |
|---|---|
| 0 | 0 |
| -1 | 10 |
| -2 | 55 |
| -3 | 69 |
| -4 | 76 |
| -5 | 80 |
| -10 | 81 |
| -20 | 91 |
| -30 | 92 |

### Crystallization

Crystallization during freezing is the formation of a systematically organized solid phase from a solution or liquid. It consists of two phases viz. nucleation and crystallization. During removal of heat, water molecules tend to combine into an ordered manner in the form of a particle. When the size of the particles is sufficient to survive and serve as a site for crystal growth, it is called nucleus. The process of formation of nucleus is called nucleation. When the size is not sufficient for the growth it is called embryo. During crystal growth an enlargement of the nucleus takes place by an orderly addition of water molecules.

### Crystal Growth

The second phase of crystallization consists of crystal growth. It requires some super cooling usually less than 0.1°C. The crystal growth occurs by the systematic addition of molecules to the crystal surface. Crystallization of water from a solution containing different solutes is limited by mass transfer and heat transfer. Water molecules move from the liquid phase and attach to this sites where the energy is

sufficiently low to provide stability. At the same time the solute must diffuse away from the vicinity of the interface towards the interior of the liquid phase. The latent heat of crystallization must be removed to sustain crystallization.

## Crystal Size

Rapidly frozen food contain ice crystals which are small and numerous. But similar specimens, which have been frozen slowly, contain few ice crystals of large size. The sizes of the completed crystal vary inversely with the number of nuclei formed. Even though freezing conditions are held constant, large differences in crystal size are sometimes noticed among different substances, different samples of the same substance and even within the same sample. Fish frozen in pre-rigor contain smaller and more numerous ice crystals than that in post rigor under similar conditions. This is attributed to the greater amount of bound water in the pre rigor samples than post rigor samples. These bindings retard the migration of free water in pre-rigor muscle and thereby encourage formation of more nucleuses.

## Location of Ice Crystals in Tissue

The location of ice crystals in tissue is a function of freezing rate, specimen temperature and the nature of the cells. Slow freezing of fish muscle generally causes ice crystals to form exclusively in extracellular areas. Although uncommon, intracellular ice crystals have been observed in some slowly frozen specimens e.g. pre-rigor cod and tissue frozen for a second time. Conditions leading to preferential extra-cellular ice crystals result in large ice crystals, maximum dislocation of water and a shrunken appearance of cells in the frozen state.

All kinds of tissues exhibit a uniform distribution of ice crystals both intracellurlarly and extracellurlarly when frozen very rapidly. In tissue, uniform crystallization is essentially synonymous with intracellular crystallization. The rate of freezing needed to produce uniform crystallization generally increases as cell size decreases. Conditions which produce intracellular crystallization result in numerous small ice crystals with minimum dislocation of water and a frozen appearance similar to the original unfrozen appearance. The food quality is usually superior than that obtain by slow freezing.

Cells contain a greater concentration of non-diffusible ions like protein than the surrounding fluids. Diffusible ions exist in unequal concentration on opposite sides of the cell membrane and the concentration of the ionic particles is greater inside the cell than outside. On this basis a lower freezing point is expected for the cell contents than the surrounding fluids. Regardless of freezing rate, crystallization is initiated primarily in the extra cellular fluid. However, crystallization of systems containing limited quantity of extracellular fluid such as pre rigor cod begins in intracellular areas.

### Freezing Techniques

There are a number of methods by which fish can be frozen. It may be either sharp (slow) freezing or quick freezing. Slow freezing is accomplished by placing the product at a low temperature and allowing it to freeze slowly usually in still air. Quick freezing is accomplished in any one or in any combination of the following four methods:

1. Immersion freezing
2. Indirect contact freezing
3. Air blast freezing and
4. Cryogenic freezing:

## Air freezing

### *Sharp freezing*

Packaged or unpackaged marine products can be frozen in air at temperature from --18 to -40°C. If "sharp" freezing is employed, air is circulated slowly or not at all and the rate of freezing is very slow. It ranges from 3-72 hour or more depending on the conditions and size of the product. Sharp freezing is not common in modern freezing operations.

### *Tunnel freezing*

Circulating cold air at high speed enables freezing to proceed at a moderately rapid rate and this method is referred to as air-blast freezing. Air-blast freezing is usually accomplished by placing the products on a mesh belt and passing it slowly through an insulated tunnel containing air at-18 to -34°C or lower, moving counter current to the product at a speed of I to 20 meter/sec. Air at -29°C and at a speed of 10-12 meter/sec, is often satisfactory, although lower temperatures are preferred.

### *Spiral Belt Freezer*

Modern designs of belt freezers are mostly based in the spiral belt freezer concept. In these freezers a product belt that can be bent laterally is used. The present design consists of a self staking and self-enclosing belt for compactness and improved air flow control. The number of tiers in the belt stack can be varied to accommodate different capanlies and line layouts. The belt is continuous. The products are placed on the belt outside the freezer where it can be supervised. As the belt is continuous it is easy for proper cleaning. Both unpacked and packed products are frozen and the freezer gives a large flexibility both with regard to product and freezing time. Both horizontal and vertical air flow can be used. Vertical airflow is more efficient.

### *Carton freezer*

This freezer consists of a number of carrier shelves which are automatically moved through the section of the unit. The operations are carried out hydraulic power with mechanical linkage to coordinate different movements. The boxes are fed automatically into the freezer on a feeding conveyor.

Air blast freezing is economical and is capable of accomodating products of different sizes and shapes. It can result in (1) excessive dyhydration of unpackaged products if conditions are not carefully controlled, and this in turn necessitates frequent defrosting of equipment and (2) undesirable bulging of packaged products which are not confined between flat rigid plates during freezing.

### *Fluidized-Bed Freezing*

Marine products of small size like prawns can be fluidized by forming a bed of prawns on a mesh belt and then forcing air upward through the bed at a rate sufficient to partially lift or suspend the particles. If the air used for fluidization is sufficiently cooled, freezing can be achieved at a rapid rate. An air velocity of at least 2 meter/sec. or more is necessary to fluidize the particles and an air temperature of - 35°C is common. The bed depth depends on ease of fluidization and this in turn depends on size, shape and uniformity of the particles. A bed depth of slightly more than 3 cm is suitable for small prawns where as a depth of 20 to 25 cm can be used for non-fluidizable products such as fillets. In this instance since fluidization is not involved a more proper name is "through-flow air freezing. It will take about 30-35min to bring down temperature from 30°C to –18°C for fish fillets up to 3 cm thick. Fluidized bed freezing has proven successful for many kinds and sizes of products. The best results are obtained with products that are relatively small and uniform

in size.

Some fluidized-bed freezers involve a two stage freezing technique wherein the first stage consists of an ordinary air-blast freezing to set the surface of the product and the second stage consists of fluidized bed freezing.

The advantages of fluidized bed freezing as compared to air- blast freezing are (1) more efficient heat transfer and more rapid rates of freezing and (2) less product dehydration and less frequent defrosting of the equipment. Dehydration loses of about 1% have been reported during fluidized bed freezing of prawns. The short freezing time is apparently responsible for the small lose of moisture.

The major disadvantages of fluidized-bed freezing is that large or nonuniform products cannot be fluidized at reasonable air velocities.

## Plate Freezing

Fish products can be frozen by placing them in contact with a metal surface cooled by expanding refrigerants. Double contact plate freezers are commonly used for freezing fish/ prawn blocks. This equipment consists of a stack of horizontal cold plates with intervening spaces to accommodate single layers of packaged product. The filled unit appears like a multi layered sandwich containing cold plates and products in alternating layers. When closed, the plates make firm contact with the two major surfaces of the packages, thereby facilitating heat transfer and assuring that the major surfaces of the packages do not bulge during freezing. Vertical plate freezers are also in use especially onboard fishing vessels. Contact plate freezing is an economical method that minimises problems of product dehydration, defrosting of equipment and package bulging. In this method the packages must be of uniform thickness. A packaged product of 3 to 4 cm thickness can be frozen in I to 1.5 hour when cooled by plates at -35°C. Freezing times are extended considerably when the package contains a significant volume of void spaces.

## Liquid Immersion Freezing

Liquid immersion freezing or direct immersion freezing is accomplished when a product is frozen by immersion in or by spraying with a freezant that remains liquid throughout the process. This technique is occasionally used for fish and prawns. Liquid immersion freezing can result in moderately rapid freezing. Freezants used for liquid immersion freezing should be non-toxic, inexpensive, stable, reasonably inert, and should have a low viscosity, low values of vapour pressre and freezing point and reasonably high values for thermal conductivity. Freezants should have a low tendancy to penetrate the product, little or no undesirable effects on organoleptic properties and require little effort to maintain desired standards for sanitation and composition. Aqueous solution of propylene glycol, glycerol, sodium chloride, calcium chloride and mixtures of sugars and salt have been used as freezant.

## Cryogenic Freezing

Cryogenic freezing refers to very rapid freezing by exposing food products to an extremely cold freezant undergoing change of state. The fact that heat removal is accomplished during a change of state by the freezant is used to distinguish cryogenic freezing from liquid immersion freezing. The most common food grade cryogenic freezants are boiling nitrogen and boiling or subliming carbondioxide. Boiling nitrous oxide also has been considered, but at present it is not being used commercially. Boiling CCl2F2 (freon-12) does not have sufficiently low boiling point to qualify as a true cryogenic fluid, but it is included in this category since it can provide, by the change of state principle, rates

of freezing comparable to those obtained commercially with true cryogenic freezants.

The rate of freezing obtained with cryogenic methods is much greater than that obtained with conventional air-blast freezing or plate freezing, but is only moderoately greater than that obtained with fluidized bed or liquid immersion freezing. For example, shrimp freeze in about 9 min in a commercial liquid nitrogen freezer and in about 12 min in a fluidized bed freezer.

Currently liquid nitrogen is used in most of the cryogenic food freezers. Usually liquid nitrogen is sprayed or dribbled on the product or alternatively very cold gaseous nitrogen is brought into contact with the product. None of the current commercial liquid nitrogen freezers employ the technique of direct immersion. It should be noted that the final product temperature is usually not different from that obtained during conventional methods of freezing. The following are some of the advantages of liquid nitrogen freezing.

1. Dehydration loss from the product is less than 1%.

2. Oxygen is excluded during freezing.

3. The individually frozen products undergo minimal freezing damage. Fish/prawns frozen cryogenically exhibit minimum thaw exudate and minimum damage to texture. These quality advantages are retained if the frozen storage is minimised and / or the temperature is -23°C or lower.

4. The equipment is simple, suitable for continuous flow operations, adaptable to various production rates and product sizes, or relatively low initial cost, and capable of high production rates in a minimal space.

The only disadvantage is the high operating cost and this is attributable nearly entire to the cost of liquid nitrogen.

Freezing with carbon dioxide usually involves tumbling the product in the presence of powdered or liquid carbon dioxide. This method provides most of the advantages cited for liquid nitrogen freezing. Carbon dioxide is absorbed or entrained by the product in this method. This entrapped CO2 should be removed before it is packaged in an impervious material.

In freon -12 as cryogenic freezant the material is placed on stainless steel mesh belt and conveyed through an insulated freezing chamber. Freezing is accomplished either by spraying the product with food grade CCI2F2 or by a combination of initial immersion of the product followed by spraying. In both procedures vapours are collected for reuse. Advantages for freezing in liquid freon-12 are essentially the same as those cited for liquid nitrogen. This method has an advantage of lower operating costs.

### Crusto Freezer

This is a combination of cryogenic freezing system and air blast freezing system. The equipment utilizes the possibility of a fast and efficient crust freezing of extremely wet, sticky products which can then be easily handled in a spiral belt freezer or a fludized bed freezer without deformation or breakage.

### Physical Changes during Freezing

The volume change in pure water at 0°C on conversion to ice at 0°C is about 9%. Most foods expand on freezing but to a lesser extent than pure water. The various factors that contribute to volume change upon freezing of food are:

1. Cooling of specimen prior to freezing causes contraction

2. Ice formation during freezing causes expansion
3. Cooling of ice crystals causes contraction
4. Solute crystallization causes contraction or expansion depending on the type of solutes.
5. Cooling of solute crystals present in eutectics causes contraction.
6. Solidification and cooling of non-solutes such as fat causes contraction.

The effect of ice formation predominates during freezing. A consequence of the increase in volume during freezing of food is the development of mechanical stress and hence freezing damage to food. The dislocation of water that accompanies slow freezing and re-crystallization may also cause mechanical stress. Mechanical damage to the texture of tissues during freezing is marginal in muscles because of its pliable consistency and parallel arrangement of cells. Sample size, freezing rate and final temperature of the tissue appear to influence the intensity of stress. In large tissues, outer surface freezes to solid before freezing commences in inner areas. On further freezing, the inner areas get frozen leading to considerable internal stress. The rate of freezing also influences the severity of stress. Slow freezing results in unusually great damage due to detrimental size and location of ice crystals. Rapid freezing coupled with low temperature will result in severe cracking of tissues containing large percentage of water.

**Physical Changes during Frozen Storage**

The major physical changes during frozen storage of fish are freezer burn and recrystallization. Freezer burn is a surface phenomenon which occurs in improperly packed products. Freezer burn appears as an opaque dehydrated surface. It is caused by the sublimation of ice on the surface of the muscle. The sublimation takes place when the vapour pressure of ice on the surface of fish muscle is higher than the vapour pressure of the cold store. Other factors contributing to freezer burn are air velocity in the cold store, cold storage temperature and post mortem condition of the muscle. It can be prevented or reduced by glazing the product in chilled water and air tight packaging with water impermeable packaging materials.

The ice crystals in the frozen muscle undergo transformations during frozen storage causing changes in number, size and shape. This phenomenon is called re-crystallization. During frozen storage, the ice crystals in rapidly frozen samples are found to grow slowly. The sizes of the ice crystals between rapidly frozen and slow frozen samples have almost the same size after a long storage. There are many reasons for the changes in size and shape. During storage, the reorientation of the ice crystals takes place to give a stable shape with a compact structure having smaller surface to volume ratio and lower surface energy. In frozen products, the large ice crystals may grow at the expense of small crystals. This may be caused by melting-diffusion-refreezing or sublimation-diffusion - refreezing. The net result is an increase in average crystal size, decrease in the number of crystals and decrease in surface energy of the crystalline phase. Fluctuating temperature and associated vapour pressure gradients enhance this type of re-crystallization. Also contacting crystals fuse together resulting in an increasing crystal size, decrease in number of crystals and decrease in surface energy. Each frozen product exhibits a critical temperature below which re-crystallization does not occur at a significant rate. Low and uniform temperature of frozen storage can minimize re-crystallization.

## Drip

Drip is the exudates coming out from a frozen product on thawing. Fish after freezing, frozen storage and thawing often exudates a considerable amount of drip. Drip may amount to 1 to 5% or much more. Drip loss may cause sizable financial loss. On thawing, if the drip loss is high, the frozen products appear somewhat dry and stringy. However, the relationship between texture and drip loss need not be linear upto moderate drip loss, but at high drip loss, the loss of texture is directly related. Though factors like internal pressure developed during freezing, freezing rate, size and location of ice crystals may influence thaw drip, the major factors are the quality of the raw material, abuse of frozen storage and the extent of resultant denaturation. When the quality is poor and the frozen product is stored especially at a higher frozen storage temperature for a long duration the amount of drip is found high and is almost proportional to the storage period. Very slow freezing and the development of large extracellular ice crystals also have some influence. In quick freezing the cell dehydration during freezing is minimum due to the formation of uniform intracellular and extracellular ice crystals. This causes minimum damage to the cell and consequently expects a low drip.

## Temperature Fluctuation

In good cold storage it is rare that temperature fluctuation in storage rooms exceed more than ±2°C. Temperature fluctuation has little effect on quality when the storage temperature is below -18°C. Very high temperature fluctuation may have an adverse effect on product quality.

## Quality Changes

Most of the quality changes normally attributed to the freezing process are indeed unrelated to that process. In fact, except for cases where texture is adversely affected by freezing, the frozen product is often practically indistinguishable from the fresh product when thawed immediately. However, after few months of storage, depending on product, process, packaging and storage temperature, changes are noticed. These changes are due to changes during frozen storage. The drip is very much increased by warm freezer storage temperatures. The explanation generally offered is that the high ionic strength of the solution causes rapid denaturation of proteins with poor binding of water as a consequence. This effect is not pronounced at colder freezer storage temperature because of reduced reaction rates.

The most important adverse effect on freezing and frozen storage on nutritive value may be a loss of vitamins, mostly the more labile ones such as ascorbic acid, thiamin and riboflavin vitamins are water soluble and hence some losses occur in the drip.

## Time Temperature Tolerance

Longer keeping times are recorded at colder temperatures in frozen storage shelf life studies. Many chemical reactions such as lipid oxidation, lipid hydrolysis and protein denaturation and the resultant sensory changes in texture and flavour are temperature dependent. Time temperature tolerance studies for quality changes during frozen storage showed a logarithmic relationship of storage time vs. temperature of the storage. Various studies indicated that the frozen storage temperature has pronounced influence on quality and shelf life. In general, the retention of the qualities will be better at lower temperatures and an inversely proportional shelf life.

## Freeze/Thaw Stability

Most frozen food will suffer some physical deterioration if they are subjected to thawing

and refreezing. There are often textural changes brought about by the formation and reformation of ice crystals. Fish and meat both suffer under these circumstances and cause protein denaturation. It is possible to give some protection against damage from freeze/thaw cycles by using certain stabilizers. Polysaccharides such as sucrose, sorbitol, carrageenan and modified starches exhibit such cryoprotective properties.

## Selecting a method for Freezing Fish / Prawns

The selection of a method for freezing fish / prawns should be based on cost and quality considerations. It is quite possible that a product with the lowest retail price may be rejected by the consumer for a product of better quality which has been achieved by using a superior but more costly processing method. On the other hand, it is possible that some products processed by the most economical methods may have qualities which are only slightly inferior to products processed by more expensive methods.

To properly assess the effect of freezing methods on product quality, the product must be evaluated following a treatment similar to that which it will receive commercially.

To assess the quality of frozen fish products, the product must be evaluated after the following sequence of events:

1. Pre-freezing treatments such as chilling, addition of chemicals etc.
2. Freezing,
3. Frozen storage for a commercially realistic time and temperature.
4. Thawing and also cooking. Quality information can be combined with data on freezing cost to determine which method of freezing is best for the product under consideration.

## Pre-freezing and Freezing Consideration

The quality of frozen-thawed cooked fish is influenced by a number off actors including species, composition, size, how and where caught, elapsed time between harvest and freezing, the state of rigor and quality when frozen and the details of freezing process and frozen storage.

The major problems encountered during the freeze-processing of fish are oxidative deterioration, dehydration, toughening, loss of juiciness, and excessive drip. Fish are subject to deterioration by microorganisms and by autolysis when it is unfrozen. So great care must be taken to follow sanitary practices, to promptly cool to near 0°C for preprocessing operations and to freeze without undue delay. Effective prefreezing and freezing techniques are available for controlling many of these problems except toughening and loss of Juiciness. Reasonable control of toughening and loss of juiciness can be accomplished only by storing fish for a minimal time and / or at temperatures at -18°C or lower.

Undesirable oxidative changes in fish can be minimised by (1) eliminating oxygen (2) avoiding contamination with heavy metals (oxidative catalysts) (3) adding antioxidants and (4) by using low storage temperature. Dehydration can be avoided by applying glaze and suitable protective coatings.

## Chemical treatments for fish

Antioxidants or antioxidant synergists such as butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), gallate esters, ascorbic acid etc. have been applied to fish in dip solutions or incorporated in ice glazes. Prior

to freezing, fillets are immersed for 20 sec. in a solution of 6-15% sodium chloride. Thaw exudates and cooking loses can be effectively reduced by dipping in phosphate solution prior to freezing.

## Conclusion

The rate of freezing can exert some influence on the final thawed quality. It is observed that the attainment of a product temperature of -18°C or lower in a period of two hours or less will produce satisfactory results.

Plate freezing is used exclusively for orthorhombic packages of fish. Air-blast freezing is used for many kinds of fish and shell fish when packaged individually. Excessive dehydration can occur during air-blast freezing of unpackaged items unless the freezing time, air velocity, and temperature differential are maintained at suitably low value. Liquid immersion freezing is used for freezing fish and shrimp at sea and sometimes for freezing shrimp on shore. Freezing fatty fish by immersion in brine is undesirable because it accelerates oxidation of lipids during frozen storage.

Expensive liquid nitrogen freezing is used to a limited extent in western countries for freezing fish and other sea-foods. Cryogenic methods are particularly advantageous when production is small or varied, when it is important to minimize capital investment or when cryogenic method is being used to supplement conventional freezing. Freezing by means of liquid $CC_{l2}F_2$ could become of greater importance in future because it is the least expensive cryogenic method.